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ON THE DIFFUSION OF SULPHIDES THROUGH STEEL.

BY E. D. CAMPBELL.

In 1893 the author read a paper on the diffusion of sulphide of iron through steel before the American Institute of Mining Engineers. In this paper[1] five experiments were described, in which the rapidity with which the sulphide of iron used diffused through steel at a bright red heat, was strikingly shown.

In these experiments, bars of soft steel 2.5 cm. thick, 5 cm. wide and 15 cm. long, were used. The steel had the following composition: Carbon, 0.17 per cent.; silicon, 0.00 per cent.; phosphorus, 0.11 per cent.; total sulphur, 0.074 per cent. The sulphide of iron used in the above experiments was a sample of the ordinary fused sulphide used for the generation of hydrogen sulphide; it contained 20.62 per cent. sulphur.

The first purpose of the experiments was to decide whether or not an unquestioned chemical compound could diffuse through steel at a bright red heat. The statement has been made that, because carbon will diffuse through steel at a bright red heat, the diffusing carbon must be in the elemental

[1] Trans. Am. Inst. Min. Eng., 23, 621.

condition. If we could get sulphide of iron to diffuse through steel, then the statement that, because carbon will diffuse, therefore the diffusing carbon must be in the elemental condition, is without weight. The diffusing element may or may not be in a chemically combined form.

A brief description of two of the experiments above mentioned will suffice to show the extent to which the work was carried at that time. In one case a hole 12 mm. in diameter and 30 mm. deep was drilled in one edge of one of the above described bars. This hole was filled with 10 grams of sulphide of iron, and closed by driving in a short steel plug, turned to accurately fit the hole. The bar, so prepared, was then placed in a muffle furnace, brought to a bright red heat, and maintained at this temperature for four hours. An examination of the bar showed the hole to be nearly empty, except for a thin film. Drillings taken from the bar at various points, some within less than 2 mm. of the original hole, showed no perceptible increase in the percentage of sulphur in the bar. The scale, formed by the oxidation of the iron at the temperature employed, showed portions containing 2.604 per cent. of sulphur. It was evident from this that the sulphide had diffused through the bar.

In the second case the bar was prepared like the first one, except that the hole containing the sulphide of iron, instead of being plugged, was left open, and the bar was so placed in a Hoskins muffle furnace, that the interior of the hole could be observed through a small chimney in the top of the muffle. The bar was brought to a bright red heat and the sulphide was noticed apparently to settle rapidly, almost as soon as thoroughly melted. When most of the sulphide had diffused the bar was quickly withdrawn from the furnace and quenched in water; a distinct odor of hydrogen sulphide was perceived on quenching the bar. Drillings of the bar taken in the immediate vicinity of the hole showed no increase of sulphur above that originally present.

In the fall of 1893 further experiments were undertaken to determine the conditions best suited to the diffusion. A different sample of sulphide of iron from that employed in the above experiments was used at this time. The results ob-

tained were rather unexpected for it was found that, when a bar prepared like those previously described was heated, little or no diffusion took place. The temperatures to which the bar was heated, whether oxidizing or reducing, were varied without apparently influencing the result. The work was again taken up in the fall of 1894 and experiments carried on for several months with apparently little or no better success than those of 1893. The identical bars used in the first experiments were employed, but the sulphide used failed to diffuse to any appreciable extent. It was not until the beginning of the present year that the property of diffusing through steel was found to be peculiar to an oxy-sulphide of iron instead of a normal sulphide. This peculiarity is proved and illustrated by the work described below.

A normal sulphide of iron, FeS, was prepared as follows: About 450 grams of ordinary fused sulphide was placed in a clay crucible, contained in a Hoskins gasoline furnace; the crucible containing the sulphide was covered with a crucible cover, perforated with a large hole; on top of this cover was cemented a second inverted crucible, having a hole about 20 mm. in diameter in the bottom. The second crucible extended above the top of the furnace, and through it sulphur could be introduced without disturbing the crucible containing the molten sulphide. By this means it was easy to maintain the molten sulphide in an atmosphere of sulphur for any desired length of time. Experiments made by keeping the molten sulphide in an atmosphere of sulphur for varying lengths of time showed that all oxide present was reduced, and the composition became constant when normal ferrous sulphide was obtained.

The steel, employed for the diffusion tests described in this work, was kindly furnished by Mr. M. J. Moore, chemist of the Illinois Steel Co., Joliet, Ill. A Bessemer steel billet having the following composition: Carbon, 0.10 per cent.; silicon, 0.009 per cent.; sulphur, 0.091 per cent.; phosphorus, 0.103 per cent.; manganese, 0.52 per cent., was heated and drawn down under the hammer to a thickness of 2.5 cm. and a width of 5 cm. This bar was then cut into pieces 5, 10, and 15 cm. long, weighing about 500, 1,000, and 1, 500 grams, re-

spectively. The short pieces were the ones employed in the diffusion tests to be described. The holes for containing the sulphide were in all cases drilled vertically in the narrow side of the bar; the holes were 12 mm. in diameter and 3 cm. deep, thus leaving about 6 mm. of metal on each side of the hole and 2 cm. beneath. The holes were placed at varying distances from the ends of the bar, these distances being stated under each experiment. When a hole after being filled with the sulphide, was plugged, this was done by accurately fitting a short tapered steel plug to the hole, and then driving it in with a heavy hammer. In examining the interior of a plugged hole after diffusion, it was almost always found necessary to drill out the plug, as it would be firmly welded in.

The furnace used for heating the bars was an assay muffle-furnace heated with gasoline. The muffle was 10 cm. high, 15 cm. wide, and 25 cm. long, provided at the back end with a small chimney, 10 cm. high, to increase the draught of air through the muffle when an oxidizing atmosphere was desired. Owing to the weight of the bars and thinness of the muffle bottom it was found desirable to reinforce the latter with a heavy false bottom 1 cm. thick. When an oxidizing atmosphere was desired the chimney was left open and the front of the muffle loosely closed with the door. When a reducing atmosphere was wanted the chimney was covered with a piece of mica, two or three large pieces of charcoal placed in the muffle, and the door closed and luted with fire clay. Bars heated to a bright red heat for several hours in a muffle so prepared, showed no signs of oxidation other than a slight blueing of the surface.

Experiment 1.—The hole in a bar 15 cm. long was filled with 20 grams of normal ferrous sulphide, FeS, and the bar so placed in the muffle that the open hole could be observed through the chimney. The muffle was then brought to a bright red heat, requiring thirty-five minutes. In fifteen minutes more the sulphide was observed to melt down; the temperature was maintained at a bright red with an oxidizing atmosphere for one hour and twenty-five minutes longer. The flame was then turned out and the bar allowed to cool slowly. The sulphide was found to have simply melted down

in the hole but with no evidence of diffusion. In two or three other instances where normal sulphide of iron was used in open or in plugged holes the same results were obtained.

Seeing, from Experiment 1, that the normal sulphide of iron, FeS, would not diffuse, we prepared a sub-sulphide in the following manner: 175 grams of the normal ferrous sulphide was melted in a crucible with the inverted crucible for a cover, arranged in the same manner as for making the normal sulphide. When the normal sulphide was perfectly liquid a little sulphur was added to insure complete reduction of any oxide that might be present, then very fine pure iron wire, tied up in little bundles of about 10 grams each, was dropped in. At first the iron was very rapidly absorbed, but absorption became slower, and, although the temperature was increased almost to a white heat, finally ceased, and apparently unattached bundles of wire were observed immersed in the liquid sulphide. The crucible was then drawn from the furnace and the liquid sulphide poured into a flat iron mold. This sulphide was hard, brittle, and of a steel-gray color with a slight yellow tinge. The analysis of the sulphide showed the following composition:

	Per cent.
SiO_2	0.10
Al_2O_3	1.66
Fe	75.59
S	22.66

Assuming the sulphur and iron to be combined as a mixture of ferrous sulphide, FeS, and subsulphide, Fe_2S, the above would give:

	Per cent.
SiO_2	0.10
Al_2O_3	1.66
FeS	5.84
Fe_2S	92.41
	100.00

Experiment 2.—A bar 5 cm. long was prepared with two holes, equally distant from the center and ends; each hole was filled with 12 grams of the above subsulphide and one hole plugged. The bar was placed in the furnace upon two sup-

ports made by wrapping small pieces of iron, 2.5 cm. long, 6 mm. wide, and 4 mm. thick, with platinum foil. These supports were used to prevent any oxide, formed during the operation, from coming in contact with the muffle bottom, and also to prevent absorption by the muffle bottom of any diffused sulphide, experiments having shown that this absorption took place to a very marked degree. The bar was heated to a bright red heat in an oxidizing atmosphere for two hours and fifteen minutes. The sulphide in the open hole had sunk very slightly, while that in the plugged hole showed no sign of diffusion.

Experiments 1 and 2, having shown that neither normal ferrous sulphide, FeS, nor a subsulphide approximately Fe_2S, would diffuse, we next made an oxysulphide in the following manner: 400 grams of ordinary fused sulphide, such as is used for making hydrogen sulphide and containing 23.6 per cent. of sulphur, was ground and intimately mixed with 13 per cent. of its weight of fine magnetic oxide of iron, Fe_3O_4. This mixture was put into a fine-grained, clay crucible, and melted as quickly as possible; although the crucible was not kept in the furnace more than five minutes after the sulphide had melted, the molten sulphide was observed to have penetrated in many places completely through the crucible. The crucible was withdrawn and the sulphide poured into a cold iron mold. Although the crucible was kept in the furnace so short a time after the sulphide was melted, it absorbed almost one-half its weight of molten sulphide before the latter could be poured out. The oxysulphide obtained gave the following results on analysis:

	Per cent.
SiO_2	0.81
Al_2O_3	1.61
MnO	0.15
Fe	66.07
S	21.68
	90.32

Undetermined oxygen = 9.68 per cent.

Combining the sulphur as ferrous sulphide, FeS, and the remaining iron as ferrous oxide, FeO, gives:

	Per cent.
SiO_2	0.81
Al_2O_3	1.61
MnO	0.15
FeS	59.62
FeO	36.16
	98.46

The above calculation would make the molecular ratio of ferrous sulphide, FeS, to ferrous oxide, FeO, in the oxysulphide, 2.7 to 2. These results would indicate the probable existence of an oxysulphide of iron, Fe_3OS, derived from ferrous sulphide, FeS, by the replacement of one-half of the sulphur by oxygen. But, owing to the extreme rapidity with which this oxysulphide, when melted, diffuses through the walls of the retaining crucible, it is extremely difficult to obtain the pure oxysulphide free from unchanged normal sulphide, FeS. The properties of the sulphide obtained above are illustrated by the following experiments:

Experiment 3.—This was undertaken to show the rate and completeness of the diffusion of the above oxysulphide. A bar 5 cm. long was used with two holes, equally distant from the center and ends. Each hole was filled with 9.65 grams of oxysulphide and one of the holes tightly plugged, the other being left open so that the diffusion could be watched as it took place. The bar was supported upon the platinum supports, the open hole being directly beneath the chimney of the muffle.

9.65 grams of the same oxysulphide was placed in a small, covered, porcelain crucible, which was then placed near the bar in order to determine whether or not the oxysulphide lost weight by heat alone. The furnace was lighted and the temperature of the bar raised in an oxidizing atmosphere. The bar attained a dull red heat in thirty minutes and a full red in fifty minutes. At this time the sulphide in the open hole was observed to melt and to commence to disappear rapidly; in from ten to fifteen seconds from the time the sulphide was observed to begin diffusing, diffusion appeared to be complete, except for a small piece, a few mm. in diameter, left in the bottom of the hole. The heat was turned off five minutes

after this time, and the bar allowed to cool. On drilling into the plugged hole the sulphide appeared to have diffused practically completely. A rather thin scale of oxide was formed on the surface of the bar, and this, on removal and analysis showed 0.50 per cent. of sulphur. It will thus be seen that the oxysulphide had diffused through the steel, and the greater part of the sulphur been oxidized by the air at the temperature at which the operation was conducted. The results of the first experiments described in 1893 proved that when that sulphide diffused through steel there was practically no retention of sulphur by the metal. The oxysulphide in the porcelain crucible placed near the bar of steel, melted in the crucible but without change in weight.

Experiment 4.—This was planned to demonstrate that when diffusion of the oxysulphide takes place, the diffusion extends throughout the entire length of the bar and not merely through the thin-walled metal between the holes and the sides of the bar. A bar 10 cm. long was used with the hole 12 mm. from one end. In this hole was placed 12 grams of oxysulphide of iron, the hole being left open. At the further end of the bar a strip of sheet asbestos about 3 cm. wide was so fastened that the ends of the strip were in contact with the top and bottom of the bar for a distance of about 2 cm. The asbestos was retained firmly in position by a wire passing around it. No portion of the asbestos was within less than 6 cm. of the hole containing the oxysulphide, the object being to apply an absorbent material to two points of the bar as far removed as possible from the diffusing sulphide. If the sulphide diffused as far as this material it must have diffused through the entire bar. The bar, with the asbestos attached, was placed upon platinum supports and the temperature brought to a bright red in an oxidizing atmosphere. In forty-five minutes from the time of lighting the furnace, the bar had attained the full heat, the sulphide had melted and diffused, and the flame was turned out. The portions of the asbestos in contact with the bar, both at the top and at the bottom, were found black and to be saturated with oxide of iron due to the oxidation of the diffused sulphide.

In order to study the behavior of other sulphides than that

of iron, cuprous sulphide was made by heating pure copper wire in a crucible, covered, and treated as in the preparation of the normal sulphide of iron. When the copper was full red, sulphur was added, and the temperature raised almost to white heat with frequent additions of sulphur for a little over two hours. In this way a nearly normal cuprous sulphide was obtained, as an analysis of the product showed 78.44 per cent. of copper, the theory for the normal sulphide, Cu_2S, being 79.8 per cent.

Experiment 5.—The bar used in this experiment was 5 cm. long with the hole equally distant from the ends, and of the usual size. In this was placed 12 grams of cuprous sulphide, and the hole was plugged. The bar, placed upon platinum supports, was kept at a bright red in an oxidizing atmosphere for two hours and forty-five minutes. On drilling into the hole the cuprous sulphide was found simply to have melted down, without diffusion. The scale on the outside of the bar was analyzed, but found to contain no copper; no evidence of diffusion could be discovered.

Experiment 6.—This was made to determine whether or not the oxysulphide of iron, when mixed with cuprous sulphide, would diffuse and, if it did diffuse, whether cuprous sulphide would be carried along with it.

A bar 5 cm. long was used with two holes equally distant from the end and center. In one hole was placed 6 grams of cuprous sulphide together with 6 grams of oxysulphide of iron, both sulphides being ground and mixed before introducing into the hole, which was then tightly plugged. In the parallel hole was firmly pressed 4 grams of ignited asbestos, this hole also being plugged. The bar so prepared was raised on platinum supports and brought in an oxidizing atmosphere to a bright red heat, at which temperature it was kept for two hours. The scale which was formed on the outside of the bar, by oxidation, was much smoother and stronger than when iron alone was present. The scale was divided into three portions, that from the bottom, middle, and top of the bar, weighing respectively 25, 19, and 24 grams. On drilling into the first hole the sulphides had apparently diffused except for a lining of cuprous sulphide, Cu_2S, in the lower por-

tion of the hole. On opening the hole containing the asbestos the latter was found to be soaked for 6–7 mm. in depth, the lower portion of the asbestos being apparently unchanged. This altered portion of the asbestos was removed, weighed, and analyzed. The bar was then weighed and two holes drilled in it, one hole between the two original holes, but near the top; the drillings from these holes were mixed and analyzed to find the amount of copper retained by the bar. The distribution of the copper after the diffusion is best shown in the following table:

	Weight. Grams.	Percentage of copper.	Weight of contained copper. Grams.
Bar	400	0.026	0.106
Asbestos	6	8.06	0.483
Top scale	24	2.47	0.593
Middle scale	19	1.94	0.368
Bottom scale	25	6.91	1.730
Total			3.28

The 1.420 grams of copper unaccounted for in the above table as the difference between the total copper added and that recovered, undoubtedly constituted the lining in the lower portion of the hole. A determination of the per cent. of sulphur (2.92) in the scale showed the presence of 1.990 grams out of 2.600 grams of sulphur originally present in the sulphides. The analysis of the asbestos containing diffused sulphide, showed: iron, 24.28 per cent.; copper, 8.10 per cent.; sulphur, 9.98 per cent. If the iron shown in this had been derived from the oxysulphide diffusing without decomposition and the copper from cuprous sulphide, also diffusing without change, then the theoretical percentage of sulphur which would have accompanied the amount of iron and copper shown by analysis, would have been 10.12 per cent., whereas that actually found was 9.98 per cent. The latter figure would go to prove almost conclusively that not only does the oxysulphide of iron diffuse unchanged but that the cuprous sulphide passes also without decomposition through the steel.

Experiment 7.—This experiment, like No. 4, was intended to show that when diffusion of cuprous sulphide was brought

about by means of the oxysulphide of iron the diffusion also took place throughout the entire length of the bar. The bar used was 10 cm. long with a hole 12 mm. from each end, thus leaving 5 cm. of steel between the two holes. In one hole was placed 6 grams of copper sulphide with 6 grams of oxysulphide of iron, both ground and mixed, and the hole then plugged; the other hole was filled with ignited asbestos and then plugged. The bar, raised upon platinum supports, was brought in an oxidizing atmosphere to a bright red heat and kept here for three hours. Upon opening the first hole the sulphides were found to have nearly all diffused. The upper part of the asbestos was found to be converted into a hard, dark-colored mass, weighing 1.2 grams and containing 0.276 gram of copper, thus demonstrating the distance to which the copper sulphide may be carried by the diffusing oxysulphide of iron.

On sawing a vertical section through the hole originally containing the sulphides, it was found to be lined in the lower portion with cuprous sulphide, Cu_2S. On polishing this section, etching, and examining microscopically, the outline of the original hole appeared to be perfectly sharp, and there was no evidence that the steel had been attacked by the sulphides which must have entered the metal at this point.

The next sulphide operated upon was that of nickel. This was prepared by heating pure nickel wire under the same conditions as those used in making cuprous sulphide. The metal was heated and kept in an atmosphere of sulphur until it had taken up all the sulphur with which it would combine. Several experiments proved that when nickel is heated with sulphur, and the sulphide produced kept melted in an atmosphere of sulphur, the sulphide, Ni_4S_3, is the result.

Experiment 8.—To determine whether nickel sulphide, like cuprous sulphide, could be made to diffuse by mixing it with oxysulphide of iron. The bar used was 5 cm. long prepared with two holes, as in Experiment 6, one filled with asbestos and plugged, the other with 6 grams of nickel sulphide and 6 grams oxysulphide of iron, both ground and mixed before being placed in the hole, which was afterwards plugged. The bar, upon platinum supports, was heated in

the usual manner and kept at a bright red for two hours and fifty minutes. On drilling into the hole, practically all of the nickel sulphide seemed to have remained in it after melting down. The scale formed on the bar was divided into two parts, that from the lower and that from the upper portion of the bar, the scale from the lower portion weighing 24 grams and showing 0.26 per cent. of nickel or 0.062 gram, while that from the upper portion, 23 grams in weight, gave 0.10 per cent. of nickel or 0.023 gram; thus it will be seen that although there was 4.26 grams of nickel in the nickel sulphide used, only 0.085 gram diffused through the bar. The asbestos showed no change in appearance.

The above experiments were selected from 40 diffusion tests, extending over a period of about ten months, distributed in three or four intervals during the past three years. It did not seem desirable to describe more than the above experiments as they suffice to demonstrate the peculiar property of diffusion of oxysulphide of iron, which ultimately became the object of the research. We might offer the following possible explanation of the observed phenomena. The oxysulphide being an extremely mobile liquid at the temperature at which the experiments were performed would readily be absorbed by any porous body. The rapidity of its absorption by the crucible, while being made, shows this. If steel is at all porous at a bright red heat then the oxysulphide would diffuse through these pores and be drawn rapidly into any porous absorbent material, such as asbestos or scale, from the superficial oxidation of the bar. The retention of so small an amount of copper by the bar after diffusion takes place, shows that although pores may exist in the steel, their volume is extremely minute compared with that of the metal. The tendency of the diffusing sulphide to accumulate towards the lower part of the bar would show the influence of gravity on the diffusing sulphide, and that it diffuses in a liquid and not gaseous form.

The fact that pure cuprous sulphide will not diffuse, although a mixture of pure cuprous sulphide and oxysulphide of iron will do so can be explained only on the assumption that pure cuprous sulphide is not sufficiently mobile when

liquid to enter the extremely fine pores in the steel, but that mobility is increased sufficiently by diluting with the extremely mobile oxysulphide of iron, thus enabling absorption to take place, and diffusion through the bar.

The failure of the greater part of nickel sulphide, Ni_4S_3, to diffuse even when mixed with oxysulphide of iron, would clearly show the greater difficulty of obtaining this body in a sufficiently finely divided state to enter the pores of the steel.

The experimentation in the above work was carried on by my successive private assistants, W. G. Wallace, C. R. Rose, F. Thompson, and E. B. Hart, and here I acknowledge my obligations to them for the care and patience with which they have conducted the above research.

ANN ARBOR, MICH., July 11, 1896.

ON THE INFLUENCE OF HEAT TREATMENT AND CARBON UPON THE SOLUBILITY OF PHOSPHORUS IN STEELS.

BY E. D. CAMPBELL AND S. C. BABCOCK.

It has been well known for some time that the brittleness of steel, due to the presence of phosphorus, is more marked when the percentage of carbon is high than when there is but little carbon present, and that with the same percentage of carbon the brittleness is more marked when the metal is hardened than when it is in its annealed or normal state. Since the above is true, it would seem that there must be some relationship between the carbon and phosphorus compounds in steel, and that the chemical condition in which phosphorus exists in steel is capable of being changed by varying the heat treatment. With a view to determining whether chemical evidence could be obtained to prove that phosphorus may exist in steel in at least two forms, our research was undertaken.

Three specimens of steel were used in this work :

No. I was a soft steel containing 0.10 per cent. carbon and 0.119 per cent. phosphorus.

No. II was a mild steel containing 0.37 per cent. carbon and 0.160 per cent. phosphorus.

No. III was a Bessemer steel containing 0.73 per cent. carbon and 0.114 per cent. phosphorus.

Annealed samples were obtained by placing specimens in a muffle furnace containing pieces of charcoal to prevent oxidation, bringing the whole to a bright red heat, then packing the muffle with a mixture of wood ashes and charcoal, closing everything as tight as possible, and allowing to remain till cold. The steel was considered in its normal state as it came from the mill. The hardened specimens were obtained by heating pieces in a muffle furnace to bright red heat and quenching in cold water. Samples for analysis of all these specimens except No. III hardened were obtained by drilling. The No. III hardened was reduced by pounding in a steel mortar until it was all passed through a sieve with 20 meshes to the linear inch.

The phosphorus soluble in neutral mercuric chloride is determined in the following manner: Five grams of steel together with 35 grams of finely ground mercuric chloride are introduced into an eight-ounce Erlenmeyer flask with 130 cc. water. Carbon dioxide is then passed in till all air is displaced, in order to avoid oxidation of ferrous chloride, and the flask tightly stoppered and shaken for some time until the solution of the steel is complete. The annealed and normal steels dissolve quite readily, solution usually being complete within an hour. The hardened metal is much less readily soluble, so that it is usually found best to allow the solution to stand over night before filtering. When the solution of the iron is complete, the precipitation of mercury associated with any insoluble compound is filtered out (using the pump to hasten the operation) and washed with hot water till the filtrate gives no test for ferrous iron with potassium ferricyanide. The filtrate is examined for phosphorus in solution by adding 10 cc. of a solution of ferric chloride, then adding 4 grams of sodium acetate and heating till the precipitate of basic acetate separates, carrying ferric phosphate with it. The basic acetate precipitate is dissolved in hot hydrochloric acid (1–3), washed through with hot water, concentrated, and finally boiled down with excess of nitric acid till all hydrochloric acid is oxidized. The solution of ferric nitrate thus obtained

is then diluted slightly, ammonia added in excess, cleared up with nitric acid and the phosphoric acid precipitated, with the usual precautions, with ammonium molybdate. The ferric chloride used was prepared by dissolving 8.15 grams of pure iron wire containing 0.050 per cent. phosphorus in hydrochloric acid, oxidizing by cautious addition of chloric acid, and diluting to 250 cc. 10 cc. of this solution contained 0.326 gram iron, 1 cc. free hydrochloric acid, phosphorus enough to give 0.01 gram precipitate of ammonium phosphomolybdate, for which amount allowance was made in the determinations given in the appended table.

The determination of the phosphorus insoluble in mercuric chloride, but soluble in 4-per cent. hydrochloric acid (40 cc. hydrochloric acid diluted in 1000 cc.) is made by taking filter-paper containing the precipitated and washed mercury from the above determinations, introducing into an Erlenmeyer flask and shaking well for ten minutes with 100 cc. of the cold dilute acid. The mercury and the paper are separated by filtering and washing with hot water. The filtrate is boiled down with addition, toward the last of the operation, of an excess of nitric acid, and the phosphoric acid determined, after neutralization with ammonia and subsequent acidification with nitric acid, by addition of ammonium molybdate.

The phosphorus insoluble in neutral mercuric chloride is determined by taking the washed precipitate of mercury obtained by dissolving a second sample and removing it as completely as possible from the filter-paper. The filter is charred and ignited in a porcelain crucible at as low a heat as possible. The mercury is introduced into a large combustion-boat, which is then put into a large combustion-tube and the mercury volatilized in a stream of carbon dioxide by cautiously heating the tube. The vapors of mercury are condensed by drawing the gas through a Wolff bottle containing water. After the volatilization of the mercury, the residue in the boat is added to the small portion obtained by igniting the filter-paper in a porcelain crucible, the whole treated with nitric acid (1.40), evaporated to dryness, and baked to oxidize the phosphorus thoroughly. The residue is dissolved in hydrochloric acid (1.20), filtered to remove silica, boiled down with excess of nitric

acid, and the phosphoric acid precipitated in the usual manner with ammonium molybdate. This determination gives the total amount of phosphorus insoluble in neutral mercuric chloride, from which, by subtracting the amount soluble in 4-per cent. hydrochloric acid, we obtain the amount of phosphorus insoluble in neutral mercuric chloride in 4-per cent. hydrochloric acid.

The table of results is as follows:

Steel.	Per cent. carbon.	Per cent. phosphorus.	Heat treatment.	Per cent. phosphorus soluble in neutral $HgCl_2$. A.	Per cent. phosphorus insoluble in $HgCl_2$ but soluble in 4 per cent. HCl. B.	Per cent. phosphorus insoluble in either $HgCl_2$ or 4 per cent. HCl. C.	Per cent. of the total phosphorus found in A.	B.	C.
I	0.10	0.119	A	0.014	0.060	0.044	11.8	50.4	37.0
I	"	"	N	0.020	0.054	0.044	16.9	45.4	37.0
I	"	"	H	0.015	0.049	0.055	12.6	41.1	46.2
II	0.37	0.160	A	0.044	0.072	0.045	27.5	45.0	28.1
II	"	"	N	0.030	0.103	0.028	18.7	64.1	17.5
II	"	"	H	0.005	0.052	0.104	3.1	32.5	65.0
III	0.73	0.114	A	0.045	0.065	0.005	39.4	57.0	4.4
III	"	"	N	0.027	0.063	0.024	23.7	55.2	21.0
III	"	"	H	0.001	0.030	0.088	0.8	26.3	77.1

The inspection of the above table brings out the following facts:

1. With very low percentage of carbon, the effect of heat treatment upon the solubility of phosphorus is slight, probably if carbon were entirely absent there would be no effect.

2. With increase of carbon the effect of hardening is to diminish the solubility of the phosphorus.

3. With high percentage of carbon the solubility is increased by slow cooling.

These three facts would point very strongly to the probable formation at a high temperature of a difficultly soluble compound of iron with carbon and phosphorus, which is transformed on slow cooling into an easily soluble one. Since the difference in the chemical behavior of phosphorus in hardened and annealed steels is fully as marked as is that of carbon under the same conditions, it would seem not improbable that the heat absorbed or evolved in the transformation of one

form into another might account for one of the other retardations (A_2 or A_3 of F. Osmund) in the same way that the transformation of carbon into cement carbon accounts for the recalescence A.

Further work will be done in this laboratory in order to determine, if possible, the composition of the compounds indicated in the above work, and the temperature at which the transformation of one form into another takes place.

ANN ARBOR, MICH., JULY 11, 1896.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

ON MALONIC NITRILE AND SOME OF ITS DERIVATIVES.

BY B. C. HESSE.

Malonic nitrile, prepared in 1886 by L. Henry,[1] was studied by him to but a slight extent. He showed that on distillation it did not polymerize; that with cold concentrated hydrochloric acid malonic acid was readily formed; whereas in sealed tubes at 150°, it was split into chloracetic acid and carbon dioxide. With ammoniacal silver nitrate he obtained a salt which contained an amount of silver approaching that required by the formula $C_3Ag_2N_2$. So far as has been recorded syntheses by means of the salts of malonic nitrile have not been made.

The work to be described in the following pages was carried out under the supervision of Professor Nef of this university. Its object is to study some of the derivatives of malonic nitrile and to ascertain, if possible, whether in its salts the metal is bound to nitrogen or to carbon. Judging from the work on acetoacetic ester and its congeners as well as that on malonic ester, the 1.3 diketones and the nitroparaffins, it seemed quite unlikely that the metal is bound to carbon. That it is bound to nitrogen appears very probable because of the work on prussic acid and the cyanides.[2]

Cyanacetamide.

Preparation.— Cyanacetamide was prepared according to Van't Hoff's method[3] from cyanacetic ester and aqueous am-

[1] Compt. Rend., **102**, 1394. [2] Nef, (1895): Ann. Chem. (Liebig), **287**, 265-359.
[3] Van't Hoff, (1874): Ber. d. chem. Ges., **7**, 1382.

monia. The best yield as well as the purest product is obtained by slowly pouring cyanacetic ester (one molecule) into two molecules of 28-per cent. ammonia water, both reagents being at 0°. The ester dissolves and the amide soon separates out as a closely felted mass of crystals; the mass is now cooled to —15° and transferred to a Hirsch funnel, washed with ice-water until the odor of ammonia is only slight, spread on clay plates, dried in the air and finally at 100°. The yield varies from 70 to 75 per cent. of the theory.

Properties.—Thus prepared, cyanacetamide is a white substance crystallizing in hexagonal plates, melting without decomposition at 120°. It cannot be distilled either at ordinary or at reduced pressure without decomposition. It is soluble in 6.5 parts of cold water, 55 parts of cold alcohol, and is not very soluble in ether, chloroform or ligroïn. It dissolves in caustic soda solution with slow evolution of ammonia.

The fact that cyanacetamide is less soluble in alcohol than in water suggested that alcoholic ammonia would give a better yield. This is not the case, since with two molecules of a 16-per cent. alcoholic ammonia only 28 per cent. of the theoretical yield of the amide was formed, while with one molecule of alcoholic ammonia no separation whatever took place.

The clear solution of the ester in the aqueous ammonia followed by precipitation of amide has suggested the existence of an intermediate unstable addition-product which by loss of alcohol yields amide. This view has apparent support, at least, in the fact that the yield with alcoholic ammonia is only one-third of that obtained in the aqueous solution, although the solubility in water is very nearly ten times greater than in alcohol. The reason for this may be that in alcoholic solutions loss of alcohol by this addition-product with subsequent formation and precipitation of amide is prevented by the surrounding alcohol, a condition of things not found in the aqueous solution.

Sodium Cyanacetamide.—Dry cyanacetamide suspended in dry and alcohol-free ether is not attacked by sodium. On adding a few drops of alcohol reaction sets in at once, a light yellow salt being formed. It is necessary to add a few drops

of alcohol from time to time. The reaction being completed the salt is removed from the ether and dried over paraffin *in vacuo*.

On analysis 0.4199 gram substance gave 0.2911 gram Na_2SO_4.

	Calculated for $C_3N_2H_3NaO$.	Found.
Na	21.70	22.48

Two atoms of sodium cannot be taken up.

The monosodium salt in chloroform suspension readily reacts with bromine, but the reaction-products were not further investigated.

Dibromcyanacetamide, $Br_2C\begin{matrix}CN\\ C{=}O\\ NH_2\end{matrix}$.

Cyanacetamide in cold aqueous solution, treated with one molecule of bromine reacts at once. An oil separates, which after standing, becomes crystalline when scratched. Hydrobromic acid and ammonium bromide are also formed. The crystalline body thus obtained is not, as would be expected, monobromcyanacetamide,[1] but is the dibrom derivative. It is formed to the extent of 50 to 60 per cent. of the theory. After recrystallizing from benzene until a constant melting product was obtained, the substance was analyzed.

0.1705 gram substance gave 0.0931 gram CO_2, and 0.0156 gram H_2O.

0.2164 gram substance gave 23.0 cc. N at 743.6 mm. and 19°.

0.1656 gram substance gave 0.2558 gram AgBr.

0.2018 gram substance gave 0.3135 gram AgBr.

	Calculated for $Br_2C_3H_2N_2O$.	Found.
C	14.87	14.89
H	0.83	1.02
N	11.57	12.00
Br	66.11	65.74 ; 66.11

Dibromcyanacetamide, recrystallized from benzene, melts at 120°.5 without decomposition. Heated dry to 160° it gives off a slight amount of bromine ; at 210° the evolution of bromine is marked.

Dibromcyanacetamide is very soluble in cold ether and in

[1] *cf.* Ann. Chem. (Liebig), **280**, 334.

cold alcohol ; cold benzene dissolves but little, while boiling benzene dissolves it readily ; chloroform, cold or boiling, dissolves it more readily than does benzene ; cold or boiling ligroïn or carbon disulphide dissolves but very little.

With potassium cyanide in concentrated aqueous solution, a concentrated alcoholic solution of dibromcyanacetamide becomes warm and deposits a white crystalline substance and potassium bromide. With potassium iodide iodine is liberated.

Malonic Nitrile.

Perfectly dry cyanacetamide in fine powder, intimately mixed with an equal weight of phosphorus pentachloride, is introduced into a distilling flask, whose volume is about four times that of the mixture. The bulb is connected with a Brühl's apparatus, which is then exhausted ; the mixture is heated with a water-bath, and the reaction begins at about 90°, hydrochloric acid being given off in great quantities. When the liquid is boiling quietly and no more gas evolution takes place, the water-bath is replaced by a metal bath and the dark brown liquid is distilled *at once*. The distillate has generally to be redistilled twice in order to free it from traces of oxychloride of phosphorus. The yield of the purified product is upwards of 70 per cent. of the theory. The above proportion corresponds to 5 molecules of amide to 2 molecules of pentachloride. Proportions which allowed the formation of phosphorus oxychloride to take place to a great extent, rarely gave over 30 per cent. of the theoretical yield.

Malonic nitrile is a pure white, ice-like solid, melting at 29°, and boiling at 219°–220° at ordinary pressures, 99° at 11 mm. and 109° at 20 mm. On standing, even in the dark, it becomes colored. A specimen of Kahlbaum's preparation which was at least two years old, had become entirely black and, on attempting to distil it at ordinary pressure, it decomposed with great violence, emitting white fumes having the odor of ammonia and of prussic acid. In its freshly prepared aqueous solution malonic nitrile has a neutral reaction ; on standing for a day it becomes quite colored, and in two weeks has become brownish and acid in reaction. Malonic nitrile has an odor faintly resembling acetamide.

0.0699 gram substance gave 26.7 cc. N at 21° and 741.6 mm.

0.1403 gram substance gave 0.0393 gram H_2O, and 0.2774 gram CO_2.

	Calculated for $C_3H_2N_2$.	Found.
C	54.54	53.92
H	3.03	3.11
N	42.42	42.61

In the combustion, malonic nitrile forms a very hard charcoal, which is burned with great difficulty. This probably explains the low result for carbon.

In the cold the malonic nitrile is soluble in about 7.5 parts of water, 2.5 parts of alcohol, 5 parts of ether, 10 parts of glacial acetic acid, 10 parts of chloroform and 15 parts of benzene. It requires more than 150 parts of cold ligroïn (boiling-point 70°–80°) for solution. It can be extracted from its aqueous solutions by ether, and these ethereal solutions must be dried with sodium sulphate, as the small amount of caustic lime in the fused calcium chloride is sufficient to turn the nitrile yellow. Sodium hydrate solution extracts malonic nitrile from ether.

Malonic nitrile dissolved in the smallest quantity of water at 20° and poured into a 30-per cent. solution of sodium hydrate ($2\frac{1}{4}$ molecules) also at 20°, and this mixture at once poured into the calculated amount of 25-per cent. sulphuric acid cooled with ice, and then extracted with ether, all the malonic nitrile is recovered. The recovered substance is tinged a very slight brown, but is not contaminated enough to materially affect the melting-point, which is found to be 28°–29°.

An excess of cold concentrated caustic soda after a long time converts malonic nitrile into malonic acid and much colored amorphous substance.

An ethereal solution of malonic nitrile shaken up with a concentrated aqueous solution of sodium carbonate for a long time, turns brown and deposits a brown amorphous flaky substance. The aqueous solution does not yield malonic nitrile on acidifying; on boiling ammonia is evolved.

Malonic Nitrile and Bromine.

The action of bromine on malonic nitrile, either molten or

in aqueous solution, is complex, as oils and crystalline and amorphous solids are produced. Satisfactory observations with regard to the nature of the oils and the amorphous bodies could not be made because of the difficulties in the way of isolating homogeneous products. In the following only the crystalline bodies, which form from 20 to 25 per cent. of the reaction-products, will be described.

Monobrommalonic Nitrile, $\frac{H}{Br}>C(CN)_2$. — Ten grams of malonic nitrile dissolved in as small a quantity of water as possible, were treated with 24.8 grams (2 atoms) of bromine. The temperature of the solution rose at once, but was controlled by the tap water. After reaction had apparently ceased, the product was warmed on the water-bath until nearly all color of bromine had disappeared. The product is an oil heavier than and insoluble in water. The oil was extracted by ether and dried with sodium sulphate. On distilling off the ether a reddish brown oil remains, which when scratched becomes a magma of white crystals and red oil. The crystals were removed from the mixture and recrystallized from chloroform until a constant melting product was obtained. The yield of pure substance is small, about five grams or 25 per cent. of the theoretical.

On analysis:

0.2613 gram substance gave 45.6 cc. N at 22°.5 and 741.5 mm.

0.2182 gram substance gave 0.1981 gram CO_2, and 0.0188 gram H_2O.

0.1817 gram substance gave 0.2362 gram AgBr.

	Calculated for C_3HBrN_2.	Found.
C	24.82	24.75
H	0.69	0.91
N	19.31	19.33
Br	55.17	55.32

Monobrommalonic nitrile is a white crystalline solid melting between 65° and 66°. It is not very soluble in water or ligroïn, but is quite soluble in alcohol, ether, benzene, chloroform or carbon disulphide.

To 5 grams of monobrommalonic nitrile dissolved in 85 cc. of absolute ether were added 5.5 grams (slightly more than

one molecule) of silver nitrite, and the whole boiled for eight hours. At the end of this time the contents of the flask had a strong odor of nitrous fumes. After separation of the solid material from the ether, the latter was distilled off and the residue gave 0.8 gram of white crystalline substance melting at 118°–119°. The melting-point could not be raised by repeated crystallization. On analysis it was shown to be nearly all dibromcyanacetamide. The desired nitro-malonic nitrile had evidently not been formed.

An aqueous solution of monobrommalonic nitrile reacts at once with lead oxide, turning red and depositing lead bromide. If lead oxide be present in slight excess metallic lead is formed.

It also reacts with alkalies, lime and a silver cyanide giving off a sharp odor resembling cyanogen bromide, and amorphous red and yellow products are formed.

Dibrommalonic Nitrile, $Br_2C(CN)_2$, is prepared in a manner similar to that of the monobrom derivative. It is accompanied by much more oil and amorphous matter than is monobrommalonic nitrile, and consequently the yield is smaller. The product of the reaction is likewise an oil which is separated from the water; the water solution is extracted with ether, the ethereal solution and the oil are mixed, washed with a little water, dried with sodium sulphate and the ether distilled off. At this point a small quantity of crystals melting at 109° were obtained; the remaining oil on standing *in vacuo* over paraffin for some days partially solidified. After separating the crystals from the adhering reddish oil,[1] they were washed with much cold chloroform and finally recrystallized from boiling chloroform until the melting-point remained constant. The yield from 10 grams of nitrile is 6.5 grams, or about 17 per cent. of the theoretical.

The white crystals melting at 123°.5 to 124°, gave on analysis the following results:

0.2444 gram substance gave 0.1424 gram CO_2, and 0.0123 gram H_2O.

[1] The oil could not be made to yield any homogeneous oils or solids. It readily lost bromine on heating, liberated iodine from potassium iodide, distilled *in vacuo* with decomposition, giving a small quantity of white plates; cold or boiling alkalies did not produce cyanide, but merely gave off a sharp odor resembling that of cyanogen bromide.

0.1436 gram substance gave 16.3 cc. N at 18°.5 and 742.4 mm.

0.1165 gram substance gave 0.1951 gram AgBr.

	Calculated for $C_3N_2Br_2$.	Found.
C	16.07	15.88
H	0.00	0.56
N	12.50	12.85
Br	71.43	71.27

Dibrommalonic nitrile is quite easily soluble in alcohol, ether and boiling chloroform, and not very soluble in benzene or in ligroïn.

Silver Salt of Malonic Nitrile.—This silver salt was prepared by L. Henry[1] from ammoniacal silver-nitrate solution and malonic nitrile. He published no analytical data, but says that the amount of silver contained in it approaches that required by the formula $C_3Ag_2N_2$. This salt was prepared by pouring a cold aqueous solution of malonic nitrile (one molecule) into a cold solution of ammoniacal silver nitrate (2 molecules). The resulting white precipitate is agitated violently and set aside in a dark place for ten minutes. The salt is then filtered by means of a Hirsch funnel, washed with water until free from nitric acid, spread on clay plates and dried at 100° to 110° for several hours.

Silver determinations were made in two separate preparations and the carbon and hydrogen in a third.

0.1091 gram substance gave 0.1043 gram AgCl.

0.1326 gram substance gave 0.1293 gram AgCl.

0.6719 gram substance gave 0.3596 gram CO_2, and 0.0145 gram H_2O.

0.6999 gram substance gave 0.3790 gram CO_2, and 0.0170 gram H_2O.

0.4732 gram substance lost 0.0017 gram when heated to 110°–115° for three hours, and for three hours more to 130°–135°.

		Found.		
C	14.59	14.76		
H	0.24	0.27		
Ag			72.13	73.47

Moisture 0.36 per cent.

[1] L. Henry: Compt. Rend., **102**, 1394.

The salt is evidently a mixture of mono- and disilver malonic nitrile, for which the calculated percentages are:

	C_3HAgN_2.	$C_3Ag_2N_2$.
C	20.86	12.85
H	0.56	0.00
Ag	62.42	77.14

The analysis corresponds roughly to a mixture of about 25 per cent. of the monosilver salt, and 75 per cent. of the disilver salt; the presence of water either as such or as water of constitution is also excluded. The presence of disilver salt is shown by the behavior of the salt towards alkyl iodides.

The precipitate obtained as above described is at first white, but rapidly changes to yellow, and, after drying on a clay plate, is yellowish brown. It is soluble in an excess of ammonia from which dilute nitric acid reprecipitates it; an excess of the precipitant redissolves the salt. Heated dry to 210° it explodes with a flash of light and a slight noise, an odor resembling that of cyanogen being given off.

Silver Malonic Nitrile and Alkyl Iodides.

Diethyl Malonic Nitrile, $(C_2H_5)_2C(CN)_2$.—Silver malonic nitrile, when acted upon by ethyl iodide, pure or diluted with ether, gives diethylmalonic nitrile, ethyl isocyanide, and amorphous substances.

To 56 grams of ethyl iodide, cooled in ice, were carefully added 25 grams of silver malonic nitrile in 5 gram portions. Slight reaction takes place in the cold, the odor of isocyanide being very noticeable. This mixture is allowed to stand at the temperature of the room for seven hours, and is then heated on a bath of boiling water for twenty-one hours longer. The reaction-product was distilled with steam, the distillate extracted with ether, and the ether dried with calcium chloride; the light-brown residual oil, 4.5 grams, has an odor of isocyanide. Distillation *in vacuo* gave a liquid boiling at 91°–93° at 24 mm., which solidified on standing; after recrystallizing many times from water, 1.7 grams of a pure product (melting-point 44°) were obtained.

0.1203 gram substance gave 0.3004 gram CO_2 and 0.0926 gram H_2O.

0.0867 gram substance gave 18.0 cc. N at 22° and 747 mm.

	Calculated for $C_7H_{10}N_2$.	Found.
C	68.85	68.10
H	8.19	8.55
N	22.95	23.23

The yield of diethylmalonic nitrile is 15.6 per cent. of the theoretical.

Thirty-two grams of silver salt and 2.5 molecules of ethyl iodide, diluted with 3 volumes of absolute ether, were heated in a sealed tube at 100° for five hours, and the residue extracted with absolute ether gave finally 0.9 grams of diethylmalonic nitrile, melting at 45°, or 6.4 per cent. of the theoretical yield. The ether which was distilled off was shaken with concentrated hydrochloric acid until all odor of isonitrile disappeared; the acid solution was evaporated on the water-bath. The white deliquescent crystalline residue melted at 78° while ethylammonium chloride melts at 80° and is also deliquescent. This substance, whose weight was 0.4 gram, was therefore regarded as ethylammonium chloride. The yield is 4.3 per cent. of the total amount possible.

Besides these substances there was also formed a large amount of a reddish amorphous organic substance, probably polymerized ethyl isocyanide, which is insoluble in ether and was not further examined.

That the substance melting at 44° is diethylmalonic nitrile is shown by its conversion into diethylcyanacetamide by boiling with sodium ethylate in absolute alcohol solution, and the conversion of the latter into diethylcyanacetic and diethylacetic acids. These experiments will be described more fully further on.

Diethylmalonic nitrile is a white crystalline substance soluble in alcohol, ether, benzene, ligroïn, chloroform, acetone, and acetic ether; it is not soluble in cold water but dissolves in a small quantity of hot water, from which it crystallizes on cooling. Its aqueous and alcoholic solutions are neutral to litmus paper. It melts at 44° and is volatile with steam; boiled with alcoholic potash no ammonia or cyanide is formed.

One-half gram of the substance boiled with 15 cc. of care-

fully prepared absolute alcohol, containing two-tenths gram sodium, for twenty minutes, cooled and poured into water, extracted with ether, gave 0.45 gram of diethylcyanacetamide, which will be described later on.

One gram of diethylmalonic nitrile dissolved in 60 cc. of absolute alcohol containing 0.25 gram sodium, and allowed to stand at the temperature of the room for two hours, poured into water and extracted with ether, gave 1.1 grams of a yellow oil having a mint-like odor, and in other respects fully resembling the oil obtained by the action of ethyl iodide upon malonic nitrile and sodium ethylate in alcoholic solution. This oil will be shown later to consist of diethylmalonic nitrile and its alcohol addition-product, diethylcyanacetimidoethyl ether. This formation of imido ether from nitrile and alcohol in the presence of sodium ethylate demonstrates the additive power of the nitrile group in this compound toward alcohol and furnishes another instance of the formation of free imido ethers directly from the nitriles,[1] of which the substances described by Schmidtmann[2] are also very striking examples. The oil prepared in this way, after some time, acquired a slight odor of isonitrile, which disappeared if the flask remained uncorked for some time.

Dimethylmalonic nitrile, $(CH_3)_2C(CN)_2$.—To 70 grams of methyl iodide, cooled to —10°, were added 25 grams of silver malonic nitrile in 5-gram portions. The odor of isocyanide was soon detected and on gradually warming up to 35° the reaction became very violent. After the violence of the reaction had subsided the mixture was heated to 50° for six hours to insure completion of the reaction. The mass was now distilled with steam, the distillate extracted with ether, the ether dried, and distilled off.

The oily residue distilled at 62°–66° at 22 mm. and yielded 2.5 grams of a crystalline distillate. These crystals, after several crystallizations from ligroïn, melted at 32°.

0.1233 gram substance gave 0.0713 gram H_2O and 0.2882 gram CO_2.

[1] Nef (1895): Ann. Chem. (Liebig), **287**, 280. 322.

[2] Schmidtmann (1896): Ber. d. chem. Ges., **29**, 1193, 1174. Although Schmidtmann does not say so, yet there can be no doubt that these bodies are imido ethers.

0.1211 gram substance gave 32.9 cc. N at 22° and 737.8 mm.

	Calculated for $C_5H_6N_2$.	Found.
C	63.83	63.74
H	6.38	6.42
N	29.79	30.01

Further evidence that this substance is dimethylmalonic nitrile was obtained by converting it into dimethylmalonic acid by heating in sealed tubes with concentrated hydrochloric acid at 100° for two hours.

Dimethylmalonic nitrile is a white crystalline substance melting at 32°–32°.5, quite easily soluble in alcohol, ether, acetone, and acetic ether, not so easily soluble in chloroform, benzene, and ligroïn, and quite insoluble in water. Its alcoholic solution is neutral to litmus. Boiling with caustic soda produces no ammonia.

The formation of dialkylmalonic nitriles and of alkyl isocyanide suggests two points of attack in the silver malonic nitrile molecule, or that the compound partially decomposes into silver cyanide, and the latter reacting with the alkyl iodide produces the isonitrile. If the latter were true then there would be positive evidence as to the position of the metal in the substance since in silver cyanide the metal is bound to nitrogen.[1] This is hardly probable, since the formation of isonitrile takes place at 20°.

On the first assumption we may have two possibilities; namely, that the metal is bound to carbon or to nitrogen. The first of these is rendered unlikely because, in order to explain the formation of isonitrile, addition of alkyl iodide to the nitrile group would have to be supposed, a supposition for which there is no foundation in fact. On the second supposition the constitution to be assigned to the disilver salt would be

$$AgN : C : C : C : NAg.$$

A substance with so many consecutive double linkings would of necessity be a very reactive body.

By the addition of alkyl iodide to the double bonds between the carbon atoms the intermediate product

[1] Nef (1895): Ann. Chem. (Liebig), **287**, 269 et seq.

$$\begin{array}{ccccc} AgN : C & \cdot & C & \cdot & C : NAg \\ | & & \| & & | \\ I & & R_2 & & I \end{array}$$

would be formed which, by loss of silver iodide, would give dialkylmalonic nitrile. The formation of isocyanide would be explained by the direct replacement of the silver by alkyl or by addition of alkyl iodide to the double bonds between nitrogen and carbon with subsequent loss of silver iodide. In either case, of which the first is the more likely, the compounds

$$RN : C : C : C : NR \quad \text{or} \quad AgN : C : C : C : NR$$

would be formed which could decompose with the formation of isonitrile. The isonitrile at that temperature and in the nascent state would undergo polymerization to a great extent.[1]

It is well known that silver salts react more readily by direct replacement than do the sodium salts. Consequently, the sodium derivatives of malonic nitrile with alkyl iodide should form little or no isonitrile. As a matter of fact no isocyanide is found.

These facts render the constitution given for disilver malonic nitrile very probable.

Malonic Nitrile and Sodium.

Although Schmidtmann[2] has succeeded in isolating the pure monosodium malonic nitrile, the following attempts to prepare the disodium compound will not be without interest:

To 11.5 grams of malonic nitrile dissolved in 200 cc. of absolute ether were added 8.0 grams (2 atoms) of sodium; if the nitrile is perfectly pure and dry *no reaction* of any consequence takes place. On adding a few drops of alcohol a reaction is set up at once and continues for a long time, during which a yellowish-white heavy salt, mixed with a white and lighter substance is deposited. Whenever the evolution of gas slackens a few drops more of alcohol are added to increase the action. In all, 10 cc. of alcohol were added, an amount corresponding very nearly to 1 molecule. The salt was filtered off, washed with ether, and dried. Its weight was

[1] Nef (1895): Ann. Chem. (Liebig), **287**, 357.
[2] Schmidtmann (1896): Ber. d. chem. Ges., **29**, 1171.

27.13 grams. The ether filtrate contained less than 0.75 gram of dissolved material; hydrochloric acid precipitated nothing but sodium chloride and the filtrate from this contained a very small quantity of a brownish oil with a very penetrating odor. The total weight of the material taken is 27.5 grams and 27.13 grams of salt were obtained, so that very little, if any, of the nitrile escaped conversion into the salt.

Cyanides were not present in the salt.

Sodium determinations were made in two different preparations of this substance.

I. 0.5864 gram substance gave 0.4951 gram Na_2SO_4 = 27.38 per cent. Na.

II. 0.5432 gram substance gave 0.4712 gram Na_2SO_4 = 28.13 per cent. Na.

C_3HNaN_2	requires	26.13	per cent.	Na.
C_3Na_2N	"	41.82	" "	Na.
$NaOC_2H_5$	"	33.82	" "	Na.

The analysis as well as the appearance of the product make it likely that it is a mixture of at least two substances. At any rate, it reacts with alkyl iodides as though it contained both mono- and disodium malonic nitriles. A mixture of monosodium malonic nitrile and sodium ethylate in equivalent molecular proportions—the most probable composition of the product—could react as disodium malonic nitrile. Such a mixture contains 29.4 per cent. sodium, an amount not very different from that actually found.

The product obtained is a light yellow powder turning red on exposure to moist air. It dissolves readily in water, giving a yellow solution; it is slowly, but completely, soluble in alcohol. Its aqueous solution gives with silver nitrate at first a black precipitate, due probably to an excess of sodium ethylate. After removing the black precipitate, a white one is obtained on further addition of the reagent, having the same characteristics as described for the salt obtained from malonic nitrile and ammoniacal silver nitrate.

Decomposed by acids, the odor of prussic acid is obtained, and a brownish oil containing malonic nitrile melting at 27°–29° can be extracted by ether; with dilute sulphuric acid the

oil separates out at once, but with hydrochloric acid there is no separation of oil. Heated in dry condition the salt gives off ammonia and the charred residue contains cyanide and traces of carbonate. This formation of prussic acid by dilute acids is in favor of the view that the metal is bound to nitrogen, the regeneration of malonic nitrile not being a serious objection to this view, since it is not impossible that at the moment of liberation from its sodium salt malonic nitrile is

$$HN:C:\underset{H}{C}-C\equiv N,$$

of which the greater part rearranges to $CH_2(CN)_2$, while a small part escapes such rearrangement and decomposes, giving prussic acid as one of the decomposition-products.

The formation of cyanide by heating the dry, salt while not conclusive evidence, is at least of value as indirect evidence, since in cyanides the metal is bound to nitrogen.[1]

Sodium Malonic Nitrile and Ethyl Iodide.—Ten grams of the above mentioned salt were heated in a sealed tube with four molecules of ethyl iodide at 100° for eight hours. On opening the tube not a trace of isocyanide odor could be detected; prussic acid was present in the tube, as was shown by its odor, as well as by drawing air through the tube and then through caustic soda solution and showing the presence of the cyanide in the latter. The liquid contents of the tube were taken out and mixed with ether as long as any precipitate formed, which was then filtered out; the solid part of the contents of the tube was dissolved in water as far as possible, and the solution extracted with ether. The two ethereal solutions were mixed and dried with sodium sulphate. After distilling off the ether there remained an oil which on distilling *in vacuo* gave an oil boiling from 85° to 120° at 14 mm. and a solid which was identified as diethylcyanacetamide. The oily distillate was dissolved in ether, shaken out with sodium hydrate solution to remove any monoalkylated nitrile. The sodium hydrate solution after washing with ether, was poured into dilute sulphuric acid. The ether extract of this acid solution was only a very small quantity of an oil with a sharp odor. The ethereal solution which had been washed

[1] Nef (1895) : Ann. Chem. (Liebig), **287**, 269.

with alkali, was washed with water, dried and distilled. The distillate boiled at 87°–88° at 13 mm. and solidified in a freezing-mixture. After several recrystallizations from water it melted at 44° and possessed all the properties of diethylmalonic nitrile.

The yield was 2.5 grams, or 31.9 per cent. of the theoretical. The presence of prussic acid is probably due to the decomposition of monoethylmalonic nitrile.[1]

Sodium Malonic Nitrile and Methyl Iodide.—Eleven grams of sodium malonic nitrile and 57 grams of methyl iodide (four molecules) were heated in a sealed tube to 100° for 8 hours. The contents of the tube did not have any odor of isocyanide, but contained much prussic acid, which was verified in the same way as in the preceding experiment. The contents of the tube were treated in the same way as before with the additional operation of removing iodine from the ether by aqueous sodium thiosulphate. After drying and distilling *in vacuo*, an oil boiling from 50° to 70° at 11 mm., and a small quantity of a solid crystalline body were obtained. The oil was dissolved in ether and washed with sodium hydrate solution as before. Again on acidifying this alkaline solution and extracting with ether a small quantity of an oil with a sharp odor was obtained. The ethereal solution which had been washed with alkali, after distilling off the ether as before, left an oil which was almost colorless and solidified when placed on ice. After several recrystallizations from ligroïn it melted constantly at 32°–32°.5. It is dimethylmalonic nitrile, and the yield is 36 per cent. of the theory.

The solid crystalline body obtained during the distillation *in vacuo* was very small in quantity; it was found to be made up of two parts, one soluble in ether, and the other insoluble. Nothing was done with it because of the very small quantity formed.

THE ACTION OF CHLORFORMIC ESTERS AND OF ALKYL IODIDES UPON AN ALCOHOLIC SOLUTION OF MALONIC NITRILE AND SODIUM ALCOHOLATE.

a. The Action of Chlorformic Ethyl Ester.

Sodium Dicyanacetic Acid Ethyl Ester.—Five grams of

[1] P. Henry: Jahresbericht (Fittica), 1889, 639.

malonic nitrile dissolved in a small quantity of absolute ethyl alcohol were poured into 175 cc. of alcohol cooled to —15° and containing 1.75 grams (one atom) of sodium. To this mixture were added 8.5 grams (one molecule) of ethyl chlorformate. The temperature rose to +5°, and the liquid became turbid at once; the contents of the flask were cooled to —10° as rapidly as possible and then allowed to rise slowly to +10°. The liquid was neutral to litmus paper, although the odor of ethyl chlorformate was still noticeable. After vigorous agitation of the liquid the separated salt was filtered off and identified as sodium chloride; its weight was 1.9 grams or 90 per cent. of the theoretical yield. The alcohol was distilled off from the filtrate at 30–40° and 35 mm. pressure. The distillate was slightly acid and became turbid with silver nitrate. The residue was extracted with ether to remove the unchanged malonic nitrile. This ethereal extract contains, besides malonic nitrile, a substance which gives a yellowish precipitate directly with silver nitrate, and this precipitate when dried and heated on platinum foil leaves behind a fluffy, bluish-black residue. The precipitate is not due to sodium dicyanacetic ether, as will be shown later on.

The slightly yellowish residue, insoluble in ether, was extracted with boiling acetic ether, which left a small amount of sodium chloride undissolved. The acetic ether was removed by distillation, and the residue, weighing 4.2 grams or 70 per cent. of the theory, was almost white. It was purified once more by solution in 7 parts of warm alcohol and precipitating by 50 parts of ether; the crystalline precipitate is filtered off, washed with fresh ether, dried on a clay plate and then placed over paraffin *in vacuo* for 36 hours.

0.1863 gram substance gave 29.5 cc. N at 748.2 mm. and 24°.5.

0.1861 gram substance gave 0.3098 gram CO_2 and 0.0607 gram H_2O.

0.3728 gram substance gave 0.1640 gram Na_2SO_4.

	Calculated for $C_4H_4N_2O_2Na$.	Found.
N	17.50	17.53
C	45.00	45.40
H	3.13	3.62
Na	14.37	14.27

Sodium dicyanacetic ether has already been isolated, having been obtained by Haller[1] from sodic cyanacetic ether and cyanogen chloride. The salt obtained as above described has all the properties of Haller's salt: it is not soluble in chloroform, ether, ligroïn or benzene; it is soluble in about 8 parts of cold acetic ether, and the solubility is not much increased by heating. Heated dry an odor resembling that of isonitrile is first observed, and finally ammonia is given off; the residue does not contain cyanide. With boiling concentrated caustic soda this salt does not evolve ammonia, only when all the water has been driven off and the residue begins to fuse is ammonia noticeable. It does not react with dilute (1.5) sulphuric acid, but with concentrated acid it reacts at once. It dissolves in boiling concentrated hydrochloric acid from which it is again deposited unchanged in thick prisms upon cooling, and no ammonium or sodium chlorides could be detected in this deposit. The behavior towards caustic soda and hydrochloric acid is sufficient evidence of the extreme stability of this compound towards hydrolyzing agents and also shows the firm linking of the metal.

Silver nitrate produces a white curdy precipitate, which when dried has only a slight yellow tint. The dry salt heated on platinum foil gives off combustible gases having the odor of ethyl isocyanide; the residue is grayish and compact.

b. The Action of Methyl Chlorformate.

Sodium Dicyanacetic Acid Methyl Ester.—Five grams of malonic nitrile dissolved in a small quantity of absolute methyl alcohol were poured into 175 cc. of methyl alcohol containing 1.75 grams (one atom) of sodium and cooled to —15°. To this mixture 7.1 grams (one molecule) of methyl chlorformate were added at once. The temperature rose to 0°, but was soon lowered to —15°. The mixture became turbid almost immediately, and in a few moments the liquid was neutral. The greater part of the alcohol was recovered by distillation at ordinary pressure. The residual liquid, which had become slightly acid in reaction, was poured into water and extracted with ether, dried with calcium chloride,

[1] Alb. Haller (1890): Compt. Rend., III, 53-55.

and the ether distilled off. The residue is a reddish-brown oil which does not distil without decomposition at ordinary pressure, but at 10 mm. and 100° colorless malonic nitrile distils over. There remains in the bulb a mass of charcoal and white crystals. The reddish-brown oil from ethereal solution, on standing a few days, deposits crystals which are apparently monoclinic tablets, melting with partial decomposition at 206°. They give a neutral solution with boiling water, from which on cooling the substance separates out. Hot or cold ether does not take up much of it; hot alcohol dissolves it readily, cold does not. Aqueous caustic soda dissolves it readily, and from this solution it is precipitated by dilute sulphuric acid. A solution of sodium carbonate does not dissolve it. Boiling hydrochloric acid dissolves it and on cooling deposits it unchanged. A boiling solution of caustic soda does not give any ammonia; when fused with caustic soda it gives off ammonia. The amount of substance formed was about 0.05 gram.

The oil obtained from this ether was mainly malonic nitrile and contained in addition a substance giving directly with silver nitrate a yellowish precipitate which, when dried and heated on a platinum foil, swelled up and left a bluish-black mass, just as the similar substance formed in the case of ethyl chlorformate. It is not due to the presence of the sodium compound whose reaction-product with silver nitrate behaves very differently, as will be shown later.

The aqueous solution after extraction with ether was evaporated *in vacuo*, the residue extracted once more with ether, and finally with boiling acetic ether, leaving sodium chloride undissolved. There were obtained 2.9 grams of the sodium compound, or 53 per cent. of the theoretical yield. This salt was purified and dried in exactly the same manner as the corresponding ethyl compound.

0.3195 gram substance gave 0.1537 gram Na_2SO_4.

0.0838 gram substance gave 14.3 cc. N at 750.6 mm. and 17°.5.

0.1189 gram substance gave 0.1784 gram CO_2 and 0.0241 gram H_2O.

	Calculated for $C_5H_4N_2O_2Na$.	Found.
C	41.09	40.91
H	2.05	2.25
N	19.18	19.57
Na	15.75	15.60

This substance has already been isolated by Haller.[1] In addition to the description thereof given by him, it may be added that the salt is precipitated from its alcoholic solution by benzene, ligroïn, chloroform and ether; it is insoluble in acetic ether. Its behavior towards acids and alkalies, both cold and boiling, is the same as that of the corresponding ethyl derivative. The silver salt, obtained by treating the aqueous solution of the sodium compound with silver nitrate, when dried is slightly yellow, and when heated on platinum foil leaves a compact grayish residue.

c. The Action of Methyl Iodide.

Ten grams (one molecule) of malonic nitrile, dissolved in a small quantity of cold methyl alcohol, were poured into 500 cc. of cold absolute methyl alcohol containing 7 grams (two atoms) of sodium. After connecting the flask with a return-condenser, 49 grams ($2\frac{1}{2}$ molecules) of methyl iodide were added. The liquid warmed up spontaneously, but was cooled with tap water. After a few moments the flask was heated to 60° on a water-bath until the alkaline reaction disappeared. Total time of the reaction was about five minutes. The alcohol was distilled off at ordinary pressure until sodium iodide began to separate out. The remaining liquid was poured into much water, extracted with ether, the ether washed with sodium hydrate and then with water to remove any unchanged malonic nitrile and any monoalkylated product, and finally dried with calcium chloride. The light-brown oil remaining after distilling off the ether was distilled *in vacuo*. The distillate came over at 74°–76° and 22 mm.; its weight was 10.6 grams. This oil has a fragrant mint-like odor, is soluble in 8 parts of water, is decomposed by boiling with water or with methyl alcohol, giving an alkaline vapor. The aqueous solution on treatment with dilute hydrochloric acid deposits an oil suggesting the presence of imido ethers.

[1] Alb. Haller (1890): Compt. Rend., **111**, 53–56.

On analysis :

I. 0.0788 gram substance gave 16.5 cc. N at 19°.5 and 745 mm.

II. 0.0787 gram substance gave 16.6 cc. N at 22° and 747.4 mm.

Per cent. N found, I. 23.63; II. 23.61.

Calculated for dimethylmalonic nitrile 29.79 per cent.

Calculated for $(CH_3)_2C\begin{smallmatrix}\diagup CN\\ \diagdown C\overset{\diagup NH}{\diagdown OCH_3}\end{smallmatrix}$, 22.22 per cent.

This analysis therefore indicates the presence of about 82 per cent. of imidoether.

Methyl Dimethyl Cyanacetate, $(CH_3)_2{=}C\begin{smallmatrix}\diagup CN\\ \diagdown C\overset{\diagup O}{\diagdown OCH_3}\end{smallmatrix}$.—To prove the presence of imidoether 5 grams of the oil were dissolved in 40 cc. of water, filtered, and treated with an excess of cold hydrochloric acid. The oil which separated was filtered off, dissolved in ether, and dried with calcium chloride. On distilling *in vacuo* 2.45 grams of a colorless oil boiling at 78° and 24 mm. were obtained. The aqueous filtrate was extracted with ether, the ethereal solution washed with water, dried with calcium chloride and distilled *in vacuo*, when 0.8 gram of a colorless oil boiling from 76–78° at 20 mm. was obtained.

Nitrogen determinations were made in these oils. The oil which separated from the aqueous solution gave the following results :

I. 0.1896 gram substance gave 20.5 cc. N at 30°.5 and 741 mm.

II. 0.1647 gram substance gave 18.0 cc. N at 30° and 739 mm.

The oil extracted by ether:

III. 0.2020 gram substance gave 21.0 cc. N at 27°.5 and 741 mm.

I = 11.49 per cent.
II = 11.62 per cent.
III = 11.23 per cent.

Calculated for $(CH_3)_2 : C\begin{matrix}\diagup C \vdots N \\ \diagdown C \diagup\!\!\diagup O \\ \qquad \diagdown OCH_3\end{matrix}$, N = 11.02 per cent.

The oil is therefore the methyl ester of dimethylcyanacetic acid. The ammonium chloride obtained by evaporation of the aqueous solution corresponded to 3.74 grams of imido ether. The amount of imido ether obtained was 86 per cent. of this.

To prove that in the oil obtained by the action of methyl iodide upon the alcoholic solution of malonic nitrile and sodium methylate, the two methyl groups are bound to the same carbon atom, a portion of this oil was converted into dimethylmalonic acid by heating with an excess of concentrated hydrochloric acid in a sealed tube to 100° for two hours. Besides ammonium chloride, methyl chloride and some carbon dioxide, large quantities of a white crystalline substance soluble in ether were formed. This last substance after repeated recrystallization from water and ether, melted with decomposition and evolution of gas at 188°. These properties, as well as the following analysis, show the substance to be dimethylmalonic acid, already described by Thorne.[1]

0.1123 gram substance gave 0.1852 gram CO_2 and 0.0696 gram H_2O.

	Calculated for $C_5H_8O_4$.	Found.
C	45.45	44.97
H	6.06	6.88

d. The Action of Ethyl Iodide.

Diethyl Cyanacetimidoethyl Ether, $(C_2H_5)_2 = C\begin{matrix}\diagup CN \\ \diagdown C \diagup\!\!\diagup NH \\ \qquad \diagdown OC_2H_5\end{matrix}$.

—By acting upon malonic nitrile and sodium ethylate in alcoholic solution with ethyl iodide at 72°, the proportions and the operation being the same as in the preceding experiment, an oil giving indications of the presence of imido ethers and a solid which will be shown to be diethyl cyanacetamide were obtained.

On analysis of the oil

[1] Thorne (1881): J. Chem. Soc., 39, 544.

I. 0.1708 gram substance gave 30.6 cc. N at 23°, and 742.1 mm.

II. 0.1366 gram substance gave 24.5 cc. N at 23°.5, and 748.2 mm.

Found I. = 19.81 per cent. N; II. = 19.96 per cent. N.

Calculated for $(C_2H_5)_2 : C\begin{matrix} \diagup \\ \diagdown \end{matrix}\begin{matrix} C : N \\ C \\ OC_2H_5 \end{matrix}\begin{matrix} \\ \diagup\!\!\diagup \\ \diagdown \end{matrix}\begin{matrix} \\ NH \\ \\ \end{matrix}$, N = 16.66 per cent.

Calculated for $(C_2H_5)_2 : C : (CN)_2$, N = 22.95 per cent.

This analysis corresponds to a mixture of about equal parts of nitrile and imidoether. Since it has been shown that diethylmalonic nitrile on standing with alcoholic sodium ethylates gives an oil similar to the above it seemed probable that the formation of imidoether could be increased by retarding the reaction, thus allowing the nitrile, which may be formed, to become converted into imidoether under the influence of the unacted upon sodium ethylate.

This was verified in a special experiment where the reaction was allowed to take place at ordinary temperatures. Six hours were required to complete the reaction. From this mixture the oil was recovered as in the preceding cases and analyzed.

0.1226 gram substance gave 19.5 cc. N at 18°, and 740.3 mm. = 17.96 per cent. N.

This analysis corresponds to a mixture of 80 per cent. of imidoether and 20 per cent. of nitrile.

The almost complete conversion of this oil into imidoether was effected as follows: Twelve and one-half grams were dissolved in 180 cc. of absolute ethyl alcohol containing 0.75 gram sodium and allowed to stand at the temperature of the room for twenty-eight hours. The oil was then recovered in the usual way. Ten grams boiling at 90°–91° at 15 mm. were obtained; on redistillation, 8.2 grams boiling at 90°–91° at 15 mm. were obtained. The residue in the flask was oily without the slightest sign of a crystalline solid, which shows the absence of any diethyl cyanacetamide.

On analysis

0.2060 gram substance gave 31.7 cc. N at 23°, and 743.2 mm.

0.1644 gram substance gave 0.3888 gram CO_2, and 0.1408 gram H_2O.

	Calculated for $C_9H_{14}N_2O$.	Found.
C	64.27	64.49
H	9.52	9.51
N	16.66	17.04

Judging from the analysis and the steadiness of the boiling-point, the oil was apparently the pure imido ether. That such was not the case was shown when the oil was converted into

Diethylcyanacetic Ethyl Ether, $(C_2H_5)_2=C\begin{smallmatrix}\diagup\,CN\\ \\ \diagdown\,C\!=\!O\\ \\ \diagdown\,OC_2H_5\end{smallmatrix}$.—To 7.8 grams of the imido ether dissolved in 65 cc. of 33 per cent. alcohol were added 8 cc. (2 molecules) of concentrated hydrochloric acid. The temperature of the liquid rose somewhat, but was controlled by tap water. After a short time a considerable quantity of colorless oil separated out. The mixture was now poured into water, extracted with ether, the latter washed with sodium carbonate solution, and then with pure water. After drying, distillation *in vacuo* gave 4.0 grams of colorless oil (analyzed) boiling between 100° and 101° at 15 mm., and 3.0 grams boiling between 99° and 100° and 101°–102°.

On analysis

0.1182 gram substance gave 10.3 cc. N at 23°.5, and 739.2 mm.

0.1774 gram substance gave 0.4275 gram CO_2, and 0.1422 gram H_2O.

	Calculated for $C_9H_{15}NO_2$.	Found.
C	63.90	65.71
H	8.87	8.96
N	8.28	9.57

The oil is evidently the desired substance containing traces of another compound richer in carbon and nitrogen than itself, in all probability diethylmalonic nitrile. In order to test this 5.25 grams of the oil were dissolved in 90 cc. of

absolute ethyl alcohol containing 0.4 gram sodium, and the mixture allowed to stand at the temperature of the room for thirteen days. The liquid was now poured into water, treated with an excess of hydrochloric acid, and extracted with ether as before. The second distillation *in vacuo* yielded 3.1 grams of an oil boiling at 100–101° at 14 mm.

On analysis

0.1874 gram substance gave 14.4 cc. N at 21°, and 745 mm.

0.1630 gram substance gave 0.3816 gram CO_2, and 0.1293 gram H_2O.

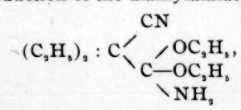
	Calculated for $C_9H_{15}NO_2$.	Found.
C	63.90	63.84
H	8.87	8.81
N	8.28	8.61

Diethylcyanacetic ether is a colorless oil with a fragrant odor, entirely different from the refreshing mint-like odor of the imido ether. It is not very soluble in water and its solubility in 33-per cent. alcohol is less than that of the imido ether.

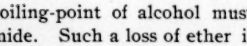
Although the diethylcyanacetimidoether described above has not been obtained in a perfectly pure state, yet it cannot be doubted that if the mixture of nitrile imido ether and alcoholic sodium ethylate had been allowed to stand longer, no unchanged nitrile would have remained. The only slightly contaminated specimen of diethylcyanacetimidoethyl ether is a colorless mobile oil possessing a fragrant and refreshing mint-like odor. It is only slightly soluble in water, and can be boiled without decomposition with water and ethyl alcohol.

Diethylcyanacetamide, $(C_2H_5)_2{=}C\begin{smallmatrix}\diagup\,CN\\ \diagdown\,C(=O)NH_2\end{smallmatrix}$.—This substance is formed in the preparation of diethylmalonic nitrile from the sodium salt and ethyl iodide in sealed tubes; in the action of ethyl iodide upon malonic nitrile and sodium ethylate in alcoholic solution; and when diethylmalonic nitrile is boiled with absolute alcohol containing 1.3 per cent. of sodium.

In this last method the alcohol had been made absolute with the greatest of care and it is not reasonable to suppose that the formation of amide is caused by the presence of water or of sodium hydrate. This is probably due to the intermediate production of the dialkylamidoether,



which at the boiling-point of alcohol must lose ethyl ether and form the amide. Such a loss of ether is not improbable since Mackenzie[1] has shown that the compound



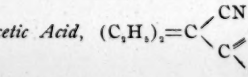
on standing over sulphuric acid in a desiccator, loses ether, and that with acid it forms benzophenone.

Diethylcyanacetamide melts at 120°, is white, and crystallizes in plates. It is soluble in alcohol, ether, and chloroform, and not very soluble in ligroïn or benzene.

0.1516 gram substance gave 0.1187 gram H_2O, and 0.3337 gram CO_2.

0.1194 gram substance gave 21.3 cc. N at 21°, and 746.9 mm.

	Calculated for $C_7H_{12}N_2O$.	Found.
C	60.00	60.02
H	8.57	8.69
N	20.00	20.05

Diethylcyanacetic Acid,  .—This substance has been made (1) from the oil obtained by the action of ethyl iodide upon malonic nitrile and sodium ethylate in alcoholic solution, (2) from diethylmalonic nitrile and (3) from diethylcyanacetamide by heating in sealed tubes with concentrated hydrochloric acid to 100° for two hours. In all cases a brownish oil floats on top of the hydrochloric acid in the tube. The oil is separated, the acid solution is mixed with

[1] (1896) Chem. News, **73**, 268.

enough water to dissolve the ammonium chloride, and shaken out with ether. The ethereal solution and the separated oil are mixed and shaken out with a solution of sodium carbonate. This carbonate solution, after being washed with fresh ether, is acidified, and again shaken out with ether; the ether washed with water, dried, and distilled. There is obtained a colorless oil boiling between 162° and 164°, at 18 mm. The oil soon solidifies to a white, hygroscopic, ice-like solid. It melts at 57° and distils undecomposed at ordinary pressure, a rather striking property of a cyanogen acid. The cyanogen group is very stable, not being affected by concentrated hydrochloric acid in a sealed tube at 120° for one hour, nor by heating with alcoholic potash in a sealed tube to 100° for three hours. A silver salt is obtained when sodium hydrate is added to a mixture of the acid and silver nitrate. The salt crystallizes from boiling water in glistening needles, which are not affected by light.

0.1847 gram substance (free acid) gave 0.1302 gram H_2O, and 0.4012 gram CO_2.

0.2534 gram substance gave 22.5 cc. N at 18°, and 749 mm.

	Calculated for $C_7H_{11}NO_2$.	Found.
C	59.57	59.23
H	7.80	7.83
N	9.93	10.15

By heating with concentrated hydrochloric acid in a sealed tube to 160° for eight hours diethylcyanacetic acid is quantitatively converted into

Diethylacetic Acid.—This acid was isolated in the same way as the preceding acid, except that it was distilled at ordinary pressure, boiling from 189–191°.[1] The portion coming over between 189°.5 and 190°.5 was analyzed.

0.1766 gram substance gave 0.1624 gram H_2O, and 0.3998 gram CO_2.

	Calculated for $C_6H_{12}O_2$.	Found.
C	62.07	61.73
H	10.35	10.22

The acid also forms the peculiar silver salt so characteristic of diethylacetic acid.[2]

[1] Saytzeff (1878): Ann. Chem. (Liebig), **193**, 351. [2] *Ibid.* p. 353.

The conversion of diethylcyanacetic acid into diethylacetic acid furnishes the proof that in all those substances yielding diethylcyanacetic acid the two ethyl groups are bound to one and the same carbon atom.

In the foregoing reasons have been given for considering that the metal in metallic derivatives of malonic nitrile is bound to nitrogen. On this basis the alcoholic solution of malonic nitrile and sodium alcoholate must be regarded as containing monosodic malonic nitrile,[1] CN—CH=C=NNa. The alkyl iodide, adding itself to the double bond between the two carbon atoms, produces, with loss of sodic iodide, monoalkylated malonic nitrile, CN—CHR—CN, which, in the presence of the excess of sodium ethylate, must immediately be converted into the sodium salt, CN—CR=C=NNa; the latter then gives, by absorption of alkyl iodide,

$$\begin{array}{l} \mathrm{CN{-}CR{-}C{=}NNa}\ (A). \\ \quad\ \ \mathrm{R}\quad\ \mathrm{I} \end{array}$$

The product (*A*) by loss of sodic iodide, yields dialkylmalonic nitrile. The formation of the monimido ether,

$$\begin{array}{l} \mathrm{CN{-}CR_2{-}C:NH}, \\ \qquad\quad\ \ \mathrm{OR} \end{array}$$

which, as has been seen, is, in the case of methyl—as well as of ethyl iodide, the chief product of the reaction, can be explained (1) on the assumption that the above intermediary product (*A*) reacts directly, as an acid iodide,[2] with the alcohol present, *i. e.*, before loss of sodic iodide takes place, or (2) on the assumption that the dialkylmalonic nitrile first formed in the reaction subsequently adds, in part, one molecule of methyl or of ethyl alcohol in view of the presence of sodium alcoholate. Since it has been shown that diethylmalonic

[1] There are no facts as yet known which in any way prove that a disodium salt of malonic nitrile or of malonic ether exists, and, on the whole, the existence of such salts seems at present improbable. We know with certainty that with an excess of sodium ethylate, cyanamide gives only the monosodium salt, $NaHN{-}CN$, notwithstanding that this compound readily gives a disilver salt, $Ag_2N{-}CN$.

The action of alkalies, mild and caustic, on malonic nitrile, as well as a careful study of the behavior of the salts of malonic nitrile and of monoalkylated malonic nitriles towards acids, acyl and alkyl chlorides, will be continued in this laboratory.

J. U. Nef.

[2] *Cf.* Nef (1895): Ann. Chem. (Liebig), **287**, 263, 315, 317–18, 343.

nitrile does actually, although very slowly, absorb ethyl alcohol with formation of the monimidoether in case some sodium ethylate is at hand, it is manifestly impossible, with the experimental data as yet available, to come to a decision as to the actual course of the generation of the monimidoether.

The formation of imido ethers, however, under the circumstances just mentioned, makes it necessary to take the possibility of their presence into consideration in all cases where the Conrad-Limpach method is applied to substances containing nitrile groups.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

ON THE "BECKMANN REARRANGEMENT."

I. CHLORIMIDOESTERS.

By Julius Stieglitz.

In 1882 Hofmann[1] discovered that acid bromamides, RCONHBr, undergo a peculiar rearrangement when heated with aqueous alkali, yielding derivatives of the isocyanates CO : NR, or their hydrobromic acid addition-products, the bromformamides, BrCONHR, the bromine atom having apparently exchanged places with the alkyl radicle R.

A similar exchange was soon afterwards observed by Beckmann[2] to occur when oximes are treated with phosphorus pentachloride or other anhydrizing reagents. Hoogewerff and Van Dorp[3] pointed out later the similarity between the reactions discovered by Hofmann and what has become known as the "Beckmann rearrangement" of the oximes. Lengfeld and Stieglitz[4] then found that the acid bromamides undergo the same rearrangement on treatment with a methyl-alcohol solution of sodium methylate, giving urethanes and other derivatives of the isocyanates.

As far as known at present, this peculiar rearrangement of acid bromamides is effected only by alkaline solutions, that of the oximes only by anhydrizing reagents; these facts would indicate that at some, perhaps early, stage of these reactions, in the one case hydrobromic acid, in the other case water

[1] Hofmann : Ber. d. chem. Ges., **14**, 2725; **15**, 408. [2] *Ibid*, **19**, 988, etc.
[3] Recueil d. Travaux chim. d. Pays-Bas, **6**, 373; **8**, 173, etc.
[4] This Journal, **15**, 215, 504.

is formed. It has become desirable to determine to what extent, if at all, the remaining hydrogen atom in the group—CONHBr is necessary for effecting the rearrangement of the acid bromamides. The hydrogen atom might influence the reaction in a number of ways, the most important of which need alone be mentioned here. The alkali might cause a direct loss of hydrobromic acid, producing the body $(RCO)N<$ with a univalent nitrogen atom, whose reactivity[1] must then be the cause of the peculiar separation of the alkyl R from the carbon atom holding the nitrogen: the very reactive univalent nitrogen atom taking the alkyl away from the carbon atom, isocyanates must result, and these have actually been obtained,[2] as the first tangible products of the reaction:

$$RC\begin{matrix}\diagup\!\!\diagup O\\ \diagdown NHBr\end{matrix} \rightarrow HBr + RC\begin{matrix}\diagup\!\!\diagup O\\ \diagdown N<\end{matrix}$$

$$R-C=O \rightarrow -C=O \rightarrow C=O$$
$$\quad | \qquad\quad | \qquad\quad ||$$
$$\quad >N \qquad -NR \qquad NR$$

This interpretation of the reaction has become yet more worthy of study because of the peculiar behavior of the acid azides $(RCO)N<\begin{matrix}N\\ ||\\ N\end{matrix}$, discovered by Curtius. These bodies when warmed even with *neutral* reagents, such as water or alcohol,[3] lose two atoms of nitrogen and give the *same* derivatives of the isocyanates which are obtained from the acid bromamides; here too one would expect the first product of the decomposition to be the body $(RCO)N<$ containing a very reactive univalent nitrogen atom, and in fact identical with the body mentioned above, and of course giving the same derivatives (*e. g.*, urethanes) of the isocyanates:

$$R-C\begin{matrix}\diagup\!\!\diagup O\\ \diagdown N<\end{matrix}\begin{matrix}N\\ ||\\ N\end{matrix} = R-C\begin{matrix}\diagup\!\!\diagup O\\ \diagdown N<\end{matrix} + N_2;$$

[1] Comparable with, and perhaps greater than, the analogous reactivity of bivalent carbon, as shown by Nef, in numerous reactions: Ann. Chem. (Liebig), **270**, 267, etc.

[2] Hofmann: Ber. d. chem. Ges., **15**, 412.

[3] Curtius: Ber. d. chem. Ges., **27**, 778: J. prakt. Chem., **50**, 289.

$$R-C=O \longrightarrow -C=O \longrightarrow C=O$$
$$\quad | \qquad\qquad\quad | \qquad\qquad\quad ||$$
$$\quad >N \qquad\qquad -NR \qquad\qquad NR$$

The rearrangement of the acid bromamides and of the acid azides, yielding, as they do, identical products, does not seem to me capable of any other interpretation equally applicable to both classes of bodies.[1]

It may be remarked here that the formation of derivatives of the isocyanates is not the only indication of the preliminary formation of the product $(RCO)N<$ with a univalent nitrogen atom, that the acid azides, $(RCO)N_3$, show. By reducing in alkaline solution, nitrogen is given off and symmetrical diacylhydrazines,[2] RCONHNHCOR, are formed, a most peculiar reaction for which no explanation has been suggested. But the reaction is easily understood, if $(RCO)N<$ is really first formed: two molecules uniting by means of the reactive univalent nitrogen atoms would give azodiacyl $(RCO)N=N(COR)$, which taking up two hydrogen atoms must yield $(RCO)NHNH(COR)$, the diacylhydrazines actually obtained. Again, when reduced in acid solution, the acid azides lose nitrogen and give acid amides, a reaction which also appears very simple according to:

$$(RCO)N<\overset{N}{\underset{N}{\|}} = (RCO)N< + N_2;$$

$$(RCO)N< + H_2 = RCONH_2.$$

In order to determine, for the reasons presented, the influence of the hydrogen atom in the acid bromamide group—CONHBr, E. E. Slosson[3] is investigating under my direction the be-

[1] *Note by J. U. Nef.*—Dr. Stieglitz having informed me of the contents of this paper, has requested me to call attention to a fact which at once struck me as being of special importance in connection with it. The rearrangement assumed here is analogous to that of the isonitriles to nitriles at 230°:

$$R-N:C< \longrightarrow N\,|\,C.R$$
$$R-(CO).N< \longrightarrow CO:NR$$

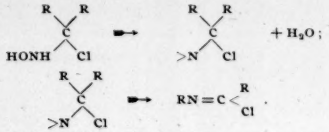
—for instance, of phenyl isocyanate, $C_6H_5N:C.$ to benzonitrile, $N\,|\,CC_6H_5$. This change is best explained on the basis that bivalent carbon at 230° possesses sufficient energy to pull off alkyl (or alphyl) from nitrogen and thus give rise to the formation of the nitrile. I have, it may be mentioned, obtained during the past year, strong indications of the existence of the NH derivatives (containing univalent nitrogen) in connection with the work on the nitroparaffins with Mr. L. W. Jones.

[2] Curtius: *loc. cit.* [3] Preliminary report and note: Ber. d. chem. Ges., **28**, 3265.

havior of the acid chloranilides and analogous bodies, which are considered to have the constitution (RCO)NClR. As yet neither Mr. Slosson nor any other chemist who has worked with these bodies has ever observed a "Beckmann rearrangement" of any acid chloralkylamine, RCO(NClR). Nor has any rearrangement of the acid dibromamides, $(RCO)NBr_2$, been yet recorded. As far as known, therefore, the presence of the hydrogen atom in —CONHBr is essential for the rearrangement of the acid bromamides by alkaline solutions, a result in perfect accord with the interpretation of this reaction given above.[1]

In pursuance of the same purpose of determining the effect of the substitution of an alkyl radicle for the hydrogen atom mentioned, I have recently begun an investigation of the chlorimidoesters, RC(NCl)OR, isomeric with the acid chloralkylamines, RCO(NClR). It was not determined by those who studied the action of alkalies on the acid bromamides, whether the metal salts first formed,[2] before rearrangement occurs, have the constitution RCO(NBrMe′) or RC(NBr)OMe′: the alkyl derivatives mentioned correspond to these two forms, and it was necessary to examine both. Chlorimidoesters have been till now known only in the carbonic acid series, Sandmeyer[3] having prepared chlorimido-

[1] *Note.*—The behavior of the oximes $R_2C{=}NOH$ in suffering rearrangement with anhydrizing reagents and the influence of stereoisomerism on their rearrangement are apparently not in accord with the interpretation of "Beckmann's rearrangement" presented. But the similarity in the behavior of the acid bromamides and the acid azides (and the isonitriles) is so striking that it may be suspected that a very close study of the oximes will reveal a similar cause of rearrangement in their case. It need only be mentioned, that when using phosphorus pentachloride, for instance, the addition of hydrochloric acid to an oxime may lead to a substance $R_2C{<}^{Cl}_{NHOH}$ which can lose water under the influence of the phosphorus pentachloride in the way required, giving by the same series of changes indicated above, acid anilide chlorides, the actual products of the reaction:



Of course this question and the problem of influence of stereoisomerism must be subjected to crucial experimental investigation.

[2] Hoogewerff and Van Dorp: *loc. cit.*; Hofmann: *loc. cit.*

[3] Ber. d. chem. Ges., **19**, 862.

ethyl and methyl carbonate, $ClN{=}C(OR)_2$, by the action of chlorine on a mixture of potassium cyanide, water and alcohol. These esters could throw little light, as yet, on the question of rearrangement, the exchange always being observed to take place between the halogen atom and an alkyl attached to the carbon atom, united to the nitrogen atom. In the case of chlorimidoesters of the type RC(NCl)OR, which I have prepared, such an exchange would be possible. Their study was inviting also, because they were at one time supposed to be intermediate products[1] in the rearrangement of alkylsynhydroximic acids, R.C(NOH)OR, by means of phosphorus pentachloride, and because there can be but little doubt that they will be found to exist in two stereoisomeric forms, the "syn" and "anti" forms:

$$\begin{array}{l} R-C-OR \\ \quad\| \\ Cl-N \end{array} \qquad \text{and} \qquad \begin{array}{l} R-C-OR \\ \quad\| \\ N-Cl \end{array}.$$

The compounds prepared by me belong perhaps to the "anti" series, but until stereoisomers have been discovered, it would not be advisable to make this distinction in naming them. As yet only the preparation of and the action of heat on chlorimidoethyl benzoate have been studied with any degree of completeness; in a later report the action of alkalies, chloranhydrides, etc., will be described.

Experimental Part.

Chlorimidoethyl Benzoate, $C_6H_5C(NCl)OC_2H_5$, can be readily obtained from the hydrochloride of benzimidoether by the action of hypochlorites. It was found best to effect the reaction in the following way: A mixture of sodium hypochlorite and free hypochlorous acid was made by passing 22 to 25 grams chlorine into a solution of 20 grams sodium hydroxide in 180 grams water, kept in a freezing-mixture. As soon as prepared—on standing decomposition is liable to occur—the hypochlorite solution was brought into a separating-funnel and 5 grams of powdered benzimidoethylether hydrochloride added in several portions, the vessel being vigorously rotated for a

[1] Werner: Ber. d. chem. Ges., **25**, 33; and **29**, 1146; Lossen: Ann. Chem. (Liebig), **281**, 298.

few minutes. Having extracted the product, an oil, with ligroïn (boiling-point 40°–60°), the extract was filtered and dried with a little solid potassic hydrate for a short time. By avoiding any absorption of moisture, the ligroïn could be nearly all distilled off on the water-bath without any decomposition of the product; the last portions of the solvent were removed in a vacuum-desiccator. A colorless, mobile oil remained, of a peculiar, not disagreeable odor; the oil showed no signs of solidifying, either on long standing or treating with a freezing-mixture or various organic solvents. Prepared in this way, the body is pure chlorimidoethyl benzoate (Analyses I and II of different preparations), and the yield is quantitative (5 grams gave 4.7 grams; the theoretical yield is 4.95 grams), according to the equation:

$$C_6H_5C(NH_2)Cl(OC_2H_5) + NaOCl = C_6H_5C(NCl)OC_2H_5 + H_2O + NaCl.$$

By using a smaller excess of hypochlorites or working with less care, some imidoethyl benzoate is liable to remain with the chlorimide. If the hypochlorite solution contains free chlorine, the ligroïn gives some chlorhydrocarbons, which remain with the chlorimide in a vacuum at ordinary temperature. The new compound was readily analyzed by means of its reaction with hydriodic acid:

$$C_6H_5C(NCl)OC_2H_5 + 2HI = C_6H_5C(NH)OC_2H_5HCl + I_2.$$

Owing to the insolubility of the chlorimide in water, it was found necessary to use an alcoholic solution for analysis: 1 to 2 grams of potassium iodide was dissolved in 2 or 3 cc. water, 20 cc. pure alcohol and about 10 drops of dilute acetic acid added, and this mixture poured on the weighed substance.

I. 0.208 gram substance required 22.31 cc. $\frac{N}{10}$ thiosulphate.

II. 0.210 gram substance required 22.50 cc. $\frac{N}{10}$ thiosulphate.

III. 0.1932 gram substance required 20.71 cc. $\frac{N}{10}$ thiosulphate.

	Calculated for $(C_9H_{10}O)NCl$.	Found.		
		I.	II.	III.
Cl	19.32	19.01	19.00	19.01

Though chlorimidoethyl benzoate, like chlorimidoethyl carbonate, is decomposed on heating at ordinary pressure, it was found to distil unchanged in a vacuum. It boils at 130°–132° (uncorr.) at 16 mm. pressure. Analysis III. and the course of the distillation show that practically no decomposition occurs, only a very slight change being observed at the end of the distillation, due to the action of the cork of the distilling-flask on the chlorimide. By fractional distillation of the mixtures which at first were sometimes obtained in preparing chlorimidoethyl benzoate, the pure substance can be easily isolated. Chlorimidoethyl benzoate is readily soluble in ligroïn, ether, chloroform and alcohol, insoluble in water and aqueous acids and alkalies. It is a comparatively stable substance, as shown by its distilling at 130° under reduced pressure. Partly owing to its insolubility in water, it is very slowly decomposed by aqueous hydrochloric acid, litmus being bleached only in the course of half an hour. After some hours benzoic ether is formed, according to the following reactions:

$$C_6H_5C(NCl)OC_2H_5+2HCl=C_6H_5C(NH_2)Cl(OC_2H_5)+Cl_2,$$

and

$$C_6H_5C(NH_2)Cl(OC_2H_5)+H_2O=NH_4Cl+C_6H_5COOC_2H_5.$$

Aqueous ammonia shows no evolution of nitrogen, while other chlorimides react instantly. Aqueous alkali leaves the oil unchanged at ordinary temperatures, even after days. The influence of solubility is shown by using the same reagents in alcoholic solution: a few drops of aqueous ammonia added evolve nitrogen; hydrochloric acid gives at once a strong evolution of chlorine. That the insolubility in water is not the only cause of the comparative stability of the chlorimide is shown by the behavior of bromimidoethyl benzoate described below.

All attempts to separate or convert ethyl chlorimidobenzoate into two stereoisomers have been as yet unsuccessful. Although the boiling-point is not perfectly constant, rising two degrees, the slight change is most likely due to the action of the stopper on the chlorimide; no fractions of different properties were obtained. Stereoisomers are now being sought

for by attempting to prepare solid chlorimidoesters, and by trying other methods of preparation. If, in preparing chlorimidoethyl benzoate, ether is used in place of ligroïn, and the solution is dried with calcium chloride, a small deposit of white needles is always observed, as a layer covering the calcium chloride. The same needles are obtained from the oil left on distilling off the ether; the solid being insoluble in ligroïn, can be separated in this way from the oil. The crystals were in all cases the hydrochloride of imidoethyl benzoate, $C_6H_5C(NH_2)Cl(OC_2H_5)$, decomposing[1] at 130° into ethyl chloride and benzamide (melting-point 128°) and giving no iodine with hydroiodic acid. Their formation is evidently due to the action of a small quantity of hydrochloric acid on the chlorimide (see above), imidoethyl benzoate hydrochloride being stable in the absence of water.

The action of heat on chlorimidoethyl benzoate was studied first to see if it would cause a rearrangement into ethyl phenylimidochlorformate,

$$\left(C_6H_5C(OC_2H_5)NCl \rightarrow ClC(OC_2H_5)NC_6H_5\right)$$

which at the temperature employed would give ethyl chloride and phenyl isocyanate;[2] the metal salts of acid bromamides, which may have an analogous constitution to that of this ether, undergo the rearrangement on heating the aqueous solution.

Four grams of chlorimidoethyl benzoate was very slowly heated in a distilling-flask connected with a condenser, and placed in a small open air-bath. As soon as the decomposition began, the air-bath was quickly removed, but the reaction once started continues very rapidly to the end, the whole mass boiling violently in a few moments. No explosion ever occurred. A strong odor of benzonitrile was perceptible both in the oily distillate and the brown, semi-solid residue; benzonitrile was extracted from both by means of ligroïn. It was fully identified by converting it into benzthiamide:[3]

$$C_6H_5CN + H_2S = C_6H_5CSNH_2.$$

[1] Pinner: Ber. d. chem. Ges., **16**, 1654, etc.
[2] Lengfeld and Stieglitz: This JOURNAL, **16**, 74.
[3] Cahours: Jahresbericht, *1847-8*, 595.

The benzthiamide obtained had all the properties of some made synthetically. On mixing the two preparations their melting-point (116°) remained constant.

Benzonitrile is the chief product (1.5 grams were obtained) of the action of heat on chlorimidoethyl benzoate. Its formation shows that the chief course of the decomposition must be

$$C_6H_5C(NCl)OC_2H_5 = C_6H_5CN + ClOC_2H_5.$$

The ethyl hypochlorite is decomposed at the temperature of the reaction, yielding hydrochloric acid and other products which were not examined. The wash-water of the distillate mentioned above gave the reactions of hydrochloric acid.

After removing benzonitrile by means of ligroïn from the brown residue left by the distillation, strong alcohol dissolved all but a small quantity of crystals, which may be called *X*. This will be discussed below. On evaporation the alcoholic solution gave white crystals embedded in a brown resin. By treatment with small portions of ether, a solid was obtained, which, after recrystallization from warm chloroform, showed the melting-point (128°) and the other properties of benzamide. On mixing with some benzamide, the melting-point did not change. Benzamide was obtained in second largest quantity ; its formation evidently is due to the action of hydrochloric acid (produced by decomposition of ethyl hypochlorite as shown above) on chlorimidoethyl benzoate, the imidoethyl benzoate hydrochloride formed first, decomposing[1] into ethyl chloride and benzamide :

$$C_6H_5C(NCl)OC_2H_5 + 2HCl = C_6H_5C(NH_2)Cl(OC_2H_5) + Cl_2;$$
$$C_6H_5C(NH_2)Cl(OC_2H_5) = C_6H_5CONH_2 + ClC_2H_5.$$

From the ethereal solution of the brown resin, no further homogeneous substance could be obtained. However, by heating the resin in a test-tube, cooling rapidly and adding water, a solution resulted which gave a plain aniline reaction with Jacquemin's reagents, but not with calcium hypochlorite solution, showing that only minute quantities of aniline could have been formed. The crystals called *X*, after repeated recrystallization from hot toluene or benzene, gave a very small quantity of a substance melting at 210°. Recrystallization

[1] Pinner : *loc. cit.*

from chloroform raised the melting-point to 227°–230° (heating rapidly). The body showed the crystal form of carbanilide (melting-point 235°), but a mixture of it with carbanilide melted 30° to 40° lower than carbanilide did. The substance is consequently not carbanilide. It could, however, be shown that it is a derivative of phenyl isocyanate (perhaps benzoylphenylcarbamide), although the amount obtained (50 mg.) was too small to be more closely studied for the present. On subliming the substance carefully in a test-tube, the odor and effect of phenyl isocyanate are unmistakable. If a few drops of water are now added, the presence of aniline is indicated by Jacquemin's reagent (calcium hypochlorite and ammonium sulphide). Carbanilide treated in the same way gave the same results. There can be no doubt, therefore, that a very small quantity of an aniline derivative is obtained by heating chlorimidoethyl benzoate at ordinary pressure. Whether it is obtained primarily from this substance or from one of its decomposition-products, will be further investigated. It is evident, however, that the chief effect of heat on chlorimidoethyl benzoate is to decompose it into ethyl hypochlorite and benzonitrile:

$$C_6H_5C(NCl)OC_2H_5 = C_6H_5CN + ClOC_2H_5,$$

a direct exchange of the phenyl group and the chlorine atom, if it takes place at all in chlorimidoethyl benzoate, occurring only to a very slight extent. It is possible that the oil under investigation is an "anti" compound,

$$\begin{array}{l} C_6H_5C\text{—}OC_2H_5 \\ \quad\quad\| \\ \quad\quad N\text{—}Cl \end{array}$$

and it remains to be seen whether a stereoisomer can be obtained, in which this exchange could occur more easily.

Bromimidoethyl Benzoate was prepared in the hope that, having a higher molecular weight, it might prove to be a solid body. It was obtained by the action of sodium hypobromite on the chloride of benzimidoether. To an excess of sodium hypobromite solution prepared from 9.2 grams bromine (8 molecules), 4.6 grams sodium hydroxide (16 molecules), and 40 grams water, 1.3 grams of the chloride of ethylimidoben-

zoate (1 molecule) was added, and the mixture shaken for a few minutes. An oil was extracted with low-boiling ligroïn, the extract dried with solid potassium hydrate, and then allowed to evaporate at ordinary temperature in a vacuum-desiccator. 1.5 grams (the theoretical yield would be 1.6 grams) of a pale yellow oil remained, which refused to crystallize. Analysis showed the body to be nearly pure bromimidoethyl benzoate.

I. 0.194 gram substance required 16.33 cc. $\frac{1}{10}$-N. thiosulphate.

II. 0.190 gram substance required 15.93 cc. $\frac{1}{10}$-N. thiosulphate.

III. 0.4486 gram substance gave 25.2 cc. nitrogen over 30 per cent. caustic potash, at 754.3 mm. and 15°.8 C.

	Calculated for $C_9H_{10}ONBr$.	Found.	
Br	35.09	33.67	33.54
N	6.14		6.53

Bromimidoethyl benzoate is far less stable than the corresponding chlorine compound. Water decomposes it gradually, reproducing the imidoether as first product. Hydrochloric acid gives bromine at once; concentrated aqueous ammonia is decomposed with evolution of nitrogen, reactions which prove that the greater stability of the chlorimide towards these reagents is not entirely due to its insolubility in them. It is probably owing to this instability, to the fact that the reaction

$$C_6H_5C(NH)OC_2H_5 + HOBr \rightleftharpoons C_6H_5C(NBr)OC_2H_5 + H_2O,$$

is reversible to some extent, that the bromimide prepared in the above manner always contains a small quantity of imidoethyl benzoate. On heating, bromimidoethyl benzoate behaves like the chlorimide, giving benzonitrile as the chief decomposition-product. As it proved to be an oil, no further experiments were made with it.

CHICAGO, *August*, 1896.

MENTHENE NITROSOCHLORIDE AND SOME OF ITS DERIVATIVES.[1]

By W. O. Richtmann[2] and Edward Kremers.

In connection with the study of the nitrosochlorides of menthene several observations have been made with regard to the melting-point of the same, that appear grossly inconsistent. Sieker, who first prepared the nitrosochloride of menthene, stated that it melted at 113° C.[3] Other observations made in this laboratory seem to indicate that the melting-point is somewhat higher. The highest melting-point of the nitrosochloride of menthene yet obtained in this laboratory was observed by Mr. Urban. It was that of a purified compound, melting at 128° C.[4]

In addition to these deviations Baeyer has made the statement that the hydrocarbon, $C_{10}H_{18}$, prepared from a tertiary menthol yields "dasselbe bei 146° C. schmelzende nitrosochlorid wie gewöhnliches menthen."[5]

It would seem either that the observations made in this laboratory were on impure material, or that Baeyer's nitrosochloride of menthene differs somewhat, though only stereometrically, from the nitrosochloride of menthene, prepared from menthene that was obtained by the dehydration of menthol.

Since the observations made in this laboratory were based upon material obtained at different times, sometimes only in very small quantities, also from menthene prepared with the aid of different dehydrating reagents, it seemed very desirable, in order to prevent the multiplication of similar incongruities, to make a thorough study of the physical constants of menthene and its nitrosochloride.

Preparation of Menthene.

A.—Mr. Helbing[6] prepared menthene by dehydrating menthol with anhydrous copper sulphate in the following manner: 500 grams of menthol and 750 grams of anhydrous copper sulphate were heated in a copper flask connected with

[1] Read at the Montreal meeting of the American Pharmaceutical Association.

[2] Fred. Pabst Fellow in Pharmaceutical Chemistry. [3] This Journal, 14, 292.

[4] *Ibid.*, 16, 395. [5] Ber. d. chem. Ges., 26, 2561.

[6] Graduation Thesis: "Nitrosochloride of Menthene and some of its Derivatives." 1894. Not published.

a reflux condenser over a free flame for from eight to ten hours. The resulting mixture was distilled with water-vapor. The oily layer of the distillate, after separation by means of a separatory funnel, was dried with anhydrous copper sulphate and then fractionated six times. The first fractionation was in fractions of 5° each; the second, third, and fourth fractionations of 1° each, and the fifth and sixth fractionations of one-half degree each. In all but the first fractionation, where an ordinary distilling-bulb was used, a "Loebel and Henninger" column was employed.

B.—The menthene employed by W. R.[1] in the second series of experiments was prepared by the dehydration of menthol in the following manner: 100 grams of menthol and 200 grams of coarsely powdered acid potassium sulphate were heated together in a round-bottomed flask, connected with a reflux condenser, for from ten to twelve hours on a paraffin-bath at a temperature of 180–200° C. The mixture thus obtained was treated in the same manner as that obtained by Mr. Helbing, as was also the resulting menthene.

C.—In a third series of experiments, menthene was obtained by means of anhydrous copper sulphate as dehydrating agent, as given under *A* of this paper. This process of dehydration was employed, now that sufficient data of the physical constants of menthene had been obtained because (1) of the larger quantities used with greater ease of manipulation; (2) the more complete dehydration of a menthol at each dehydration, and (3) the greater percentage yield of menthene.

Inasmuch as the principal object in this series of experiments was to obtain a large quantity of Δ^4-terpene-3-one, the fractionation of the menthene was not conducted with any particular care. The fractional crystallization of the nitrosochloride of menthene, however, was of some interest, and the results will therefore be recorded.

The change in the fractions of the menthene obtained by the two previously mentioned processes during the last three fractionations, as indicated by the boiling-point, specific gravity, rotatory power, and yield, are shown in the following table:

[1] Graduation Thesis. Unpublished results.

Table 1.

Fourth fractionation.					Fifth fractionation.					Sixth fractionation.				
B. P.	Sp. gr.	α.	$[\alpha]_D$.	Per-cent'ge yield.	B. P.	Sp. gr.	α.	$[\alpha]_D$.	Per-cent'ge yield.	B. P.	Sp. gr.	α.	$[\alpha]_D$.	Per-cent'ge yield.
A.														
Below 165°					Below 165°					Below 165°				
165-6°					165 -165°.5					165 -165°.5				
					165.5-166°					165.5-166°				
166-7°	0.8130			3.1	166 -166°.5					166 -166°.5				
					166.5-167°	0.8140	+22°.60	+27°.76	1.7	166.5-167°				
167-8°	0.8123	+24°.30	+28°.83	16.5	167 -167°.5	0.8113	+24°.05	+29°.60	2.3	167 -167°.5				
					167.5-168°	0.8118	+24°.01	+29°.57	15.7	167.5-168°	0.8118	+24°.48	+30°.17	14.1
168-9°	0.8128	+22°.01	+27°.08	17.8	168 -168°.5	0.8123	+23°.81	+29°.34	12.7	168 -168°.5	0.8130	+24°.20	+29°.76	11.0
					168.5-169°	0.8130	+22°.67	+27°.89	7.1	168.5-169°	0.8148	+23°.41	+28°.73	2.1
B.														
Below 165°				3.4	Below 165°					Below 165°				
165-6°	0.8103	+23°.91	+29°.51	15.4	165 -165°.5					165 -165°.5				
					165.5-166°					165.5-166°				
166-7°	0.8113	+23°.93	+29°.50	15.1	166 -166°.5	0.8106	+23°.75	+29°.30	3.2	166 -166°.5	0.8103			5.2
					166.5-167°	0.8106	+23°.88	+29°.46	5.1	166.5-167°	0.8103	+23°.98	+29°.60	7.4
167-8°	0.8136	+23°.48	+28°.86	8.9	167 -167°.5	0.8114	+23°.93	+29°.49	13.3	167 -167°.5	0.8113	+24°.04	+29°.63	15.1
					167.5-168°	0.8117	+23°.80	+29°.34	14.7	167.5-168°	0.8117	+24°.08	+29°.66	12.0
168-9°	0.8147	+22°.67	+27°.82	12.8	168 -168°.5	0.8125	+23°.45	+28°.86	12.2	168 -168°.5	0.8125	+23°.88	+29°.39	5.7
					168.5-169°	0.8140	+22°.96	+28°.81	4.3	168.5-169°	0.8135	+23°.90	+28°.76	2.7

In this table, as in all that are to follow, it is to be understood that the specific gravity and rotatory power were taken at a temperature of 20° C., and the latter in a 100-mm. tube, unless otherwise stated. The atmospheric pressure as observed during the last three fractionations by means of a mercury barometer, was as follows :

Table II.

No. of fraction.	A. mm.	B. mm.
4	735	735
2	734	735
6	739	739

Menthene Nitrosochloride.

All of the menthene nitrosochloride was prepared according to the following formula : 45 cc. of menthene, 45 cc. of glacial acetic acid, and 33 cc. of ethyl nitrite were mixed in an Erlenmeyer flask, which was placed in a freezing-mixture. While the flask is constantly being shaken in the freezing-mixture, a solution of 18 cc. of concentrated hydrochloric acid in an equal volume of glacial acetic acid is allowed to enter the flask, drop by drop, from a separatory funnel. After all of the acid in the funnel has entered the flask the entire mixture in the flask is shaken continuously for about fifteen minutes, when it is packed in a freezing-mixture and allowed to remain for an hour.

The crystals which have formed during this time are now filtered off by means of a force filter, and the mother-liquid is again placed in the freezing-mixture for the separation of more crystals. After having remained in the freezing-bath during the night, the second crop of crystals is removed, and the mother-liquid again cooled as before. In the course of a week or two a third and sometimes even a fourth crop of crystals may be obtained.

Each crop of crystals, after having been well drained on a force filter, is washed successively with small quantities of alcohol to remove the last portions of the mother-liquid. The crystals are dried on porous plates. The yield of the various crops, together with the physical constants of each, are given in the following table :

Table III.

No. of crop.	B. P. of menthene.	M. P.	$[\alpha]_D$.	Percentage yield.
A.				
1	166.5–167°			
1	167 –167°.5			
1	167.5–168°	113–114°	+20.64°	21.11
1	168 –168°.5	107–108°		21.99
1	168.5–169°			
2	166.5–167°			
2	167 –167°.5			
2	167.5–168°	106–107°		3.05
2	168 –168°.5	109–110°		4.50
2	168.5–169°			
3	all	114–115°		3.05
4	"			
B.				
1	166.5–167°	112–113°	+ 9.65°	27.36
1	167 –167°.5	112–113°	+ 9.84°	24.41
1	167.5–168°	112–113°.5	+ 8.26°	22.56
1	168 –168°.5			
1	168.5–169°			
2	166.5–167°	107–108°	Inactive	2.67
2	167 –167°.5	107–108°	"	4.34
2	167.5–168°	108–109°	"	5.05
2	168 –168°.5			
2	168.5–169°			
3	all	115–116°	Inactive	4.31
4	"	116–117°	"	3.27
C.				
1	all	112–113°	+7.234°	21.21
2	"	113–115°	Inactive	4.80
3	"	115.5–117°	"	3.00
4	"			

In order to purify the menthene nitrosochloride thus obtained it was precipitated from its solution in chloroform by means of alcohol. 18 grams of the menthene nitrosochloride were dissolved in 90 grams of chloroform. The solution was filtered and then 30 grams of alcohol were added to the filtrate. The resulting mixture was shaken frequently during ten minutes, and then the precipitated menthene nitrosochloride was filtered off with the aid of a force filter. 30 grams of alcohol were again added to the filtrate and then the process was repeated as before.

After the second crop had been removed, the filtrate was placed under the blast to evaporate for two hours. The crystals which separated were removed as before. From this filtrate still a fourth crop separated upon standing forty-eight hours. Each crop of crystals, after draining for some time on a force filter, was washed with a small quantity of alcohol, and after draining again, were placed upon a porous plate to dry.

In the table below, the yield and physical constants of each crop are given. The specimens *A* were obtained from the first crop of menthene nitrosochloride that had been prepared from menthene boiling at 167.5–168° C.; while the others, *B*, were obtained from the first crop of menthene nitrosochloride that had been prepared from menthene boiling at 167–167°.5 C.

Table IV.

Crop.	M. P.	$[\alpha]_D$.	Percentage yield.
A.			
1	113 –114°	+ 1.015°	33.47
2	108.5–109°	+16.715°	26.39
3	110 –111°	+31.234°	16.61
4	113.5–115°		2.77
B.			
1	121 –122°	— 2.4508°	32.44
2	118 –119°	+ 3.7556°	19.52
3	117 –118°	+16.4434°	24.02
4	117 –118°		1.17

It becomes evident from these figures that the menthene nitrosochloride, when prepared by the process previously given (page 765) is a mixture. Possibly the menthene from which it is prepared is itself a mixture.

It is remarkable that the first fraction (*B*), which is slightly lævogyrate has a higher melting-point than any of the other fractions, also that the second and third fractions, although differing widely in rotatory power, differ but slightly in their melting-points.

As the quantity of lævogyrate nitrosochloride of menthene obtained in series *B* was very small, the same experiments were continued in series *C*, as follows: The second crop, Table III., being entirely inactive, it was thought that per-

haps it might be a mixture of some quite strongly dextrogyrate and much more or less strongly lævogyrate nitrosochloride of menthene. The process for fractional crystallization, as given on page 767, was employed with the following results:

Table V.

Fraction.	M. P.	$[\alpha]_D$.	Percentage yield.
C.			
1	115.5–116°	Inactive	18.21
2	114 –114°.5	"	22.24
3	114 –114°.5	"	12.96
4	112.5–113°	"	8.48
5	118 –119°	"	4.65

As all of the fractions thus obtained are inactive, either the nitrosochloride is composed of inactive molecules or, if it is a mixture of dextro- and lævogyrate nitrosochlorides, as was supposed, then the process for fractional crystallization, as given above, does not serve to isolate the two forms.

The same experiment was now tried on an optically active nitrosochloride of menthene; *viz.*, crop 1, Table III.

Table VI.

Fraction.	M. P.	$[\alpha]_D$.	Percentage yield.
1	121.5–122°.5	—0.9784°	18.60
2	121 –122°	+0.9304°	10.25
3	119.5–120°	+1.7506°	11.80
4	116 –117°.5	+0.5763°	29.80

In Tables V. and VI. it is to be noticed that there is a gradual falling off of the melting-points from the first to the fourth fractions; and in Table V. a very sudden rise in the melting-point occurs in the fifth fraction. A fifth fraction was not obtained in Table VI, and consequently no observation for a like phenomenon could be made.

The first fraction of Table VI. was slightly lævogyrate, which was the variety much sought after, but it was too small in amount to work with. Only about 65 per cent. of the substance used recrystallized during this process. The experiments could not be repeated, as the remainder of crop

1, Table III., had already been employed in the preparation of nitrosomenthene.

These experiments indicate the presence of two, and possibly three, nitrosochlorides of menthene when prepared by the process given on page 765. The two known forms are the dextrogyrate and lævogyrate nitrosochlorides, while the third may be composed of inactive molecules, or the mixture of the dextro- and lævogyrate forms previously spoken of, but for the separation and isolation of which no satisfactory method has yet been found.

Menthene Nitrolbenzylamine.

A. The three purified fractions of menthene nitrosochloride, Table III., were converted into benzylamine base. 5 grams of each of the fractions, with 5.25 grams of benzylamine and 30 cc. of alcohol were heated in a round-bottomed flask connected with a reflux condenser, on a water-bath until solution was effected. The solutions were filtered and then set aside to crystallize. The crystals were separated from the mother-liquid and then recrystallized from alcohol. The melting-points of the purified products thus obtained were found to be 106°.5, 105°.5, and 105°.5, respectively. In an approximately 5-per cent. solution each was found to be optically inactive.

It is of interest to note that the menthene nitrosochlorides, differing by at least 30°, should all yield an optically inactive benzylamine base. It would be less surprising if the loss of optical activity had occurred in the dehydration of menthol to menthene or in the preparation of the nitrosochloride from the latter.

Nitrosomenthene.

Nitrosomenthene was prepared by heating 50 grams of menthene nitrosochloride with 250 cc. of a 10-per cent. alcoholic potash solution, in a round-bottomed flask, connected with a reflux condenser, on a water-bath, for from one to one and one-half hours. The resulting mixture was filtered, and the residue washed with alcohol to remove all the soluble portion. Water was now added to the filtrate to precipitate the nitrosomenthene. The mixture was allowed to stand for

twelve hours. The yellow flocculent precipitate, which had risen to the surface, was collected, washed with a small quantity of dilute alcohol, and drained with the aid of a force filter.

The nitrosomenthene thus obtained was very impure and was purified—*A*, by two recrystallizations from hot alcoholic solution; and *B*, by distillation with water-vapor—and collected in fractions.

No determination of the physical constants of the purified nitrosomenthene *A* were made. Those of the four fractions of *B* are given in

Table VII.

Fraction.	M. P.	$[\alpha]_D$.	Yield.
1	62 –64°	—9.123°	About 25 per cent.
2	63.5–64°.5	—3.655°	" 25 " "
3	64 –65°	—4.683°	" 25 " "
4	64.5–65°	—4.7915°	" 25 " "

The first and second fractions were impure, as shown by their color, which was somewhat yellowish, while the third and fourth fractions were pure white; also by their somewhat lower melting-points, and varying specific rotatory power.

It was of interest to know whether the differences in the physical constants of menthene nitrosochloride would cause similar differences in those of the nitrosomenthene. In order to make these observations, nitrosomenthene was prepared from the purified menthene nitrosochloride (see Table IV.). The resulting observations are given in the following tables: Table VIII. giving the physical constants of the nitrosomenthene before, and Table IX. after recrystallization from alcohol:

Table VIII.

Fraction.	M. P.	$[\alpha]_D$	Yield.
1	67 –68°	—1.253°	86.5 per cent.
2	67 –68°	—3.186°	85.9 " "
3	66.5–67°.5	—6.717°	85.2 " "

Table IX.

Fraction.	M. P.	$[\alpha]_D$.	Yield.
1	67 –67°.5	—6.414°	47.8 per cent.
2	67 –67°5	—10.225°	49.2 " "
3	66.5–67	—10.148°	48.7 " "

A comparison of Tables IX. and IV. shows that the difference in melting-points is practically lost, but that the sign of rotation of the menthene nitrosochlorides is reversed in splitting off the hydrochloric acid, and that the greater the positive rotation of the nitrosochloride the greater the negative rotation of the nitrosomenthene. An inactive nitrosomenthene was obtained from inactive menthene nitrosochloride, Table V. The melting-point was the same as that of the specially optically active variety; *viz.*, 65–67°. The same process as given under (*B*) was employed.

Menthylamine Nitrate.

The menthylamine was prepared by the reduction of nitrosomenthene with acetic acid and zinc dust. The nitrate of the base was separated by means of sodium nitrate, but for some reason only a very small quantity was obtained (about 10 grams from 100 grams of nitrosomenthene). This was too small a quantity to proceed with for experimentation on the alcohol $C_{10}H_{18}O$, which compound we had expected to obtain from the menthylamine nitrate.

Ketone, $C_{10}H_{18}O$.

15 grams of purified nitrosomenthene were dissolved in 30 cc. of concentrated hydrochloric acid, to which was added 30 cc. of water. The mixture was heated in a round-bottomed flask, connected with a reflux condenser, on a water-bath, for fifteen minutes, until the oily layer ceased to separate. The mixture was distilled with water-vapor. The purified oil was separated from the water and then dried with anhydrous sodium sulphate. The oil was of a light straw color, but became darker very rapidly on standing, and had a decided odor of mint. The physical constants of the oil are given in the following table:

Table X.

B. P.	Percentage yield.	Sp. gr.	α.	$[\alpha]_D$.
Below 205°	6.3			
205–206°	10.0	0.9148		
206–207°	37.1	0.9157	—1.2063°	—1.3173°
207–208°	40.2	0.9163	—1.2083°	—1.3189°
208–210°	1.2			
210–212°	1.6			
212–215°	1.2			
215–218°	0.8			
218 +	1.4			

The inactive nitrosomenthene obtained from the inactive menthene nitrosochloride was also converted into the ketone. The physical constants of the main fraction, together with those of the corresponding fraction of the ketone from the general source are given in

Table XI.

Source.	B. P.	Sp. gr.	α.	$[\alpha]_D$.
Mixed NOCl's	207–208°	0.9163	—1.2063°	—0.3173°
Inactive NOCl's	207–208°	0.9159	+0.3938°	+0.4299°

A slight difference in the specific rotatory power will be noticed. The one being dextro- and the other lævogyrate.

Upon comparison, it will be seen that the boiling-point of this ketone, $C_{10}H_{18}O$, as given above, is somewhat lower than that observed by Kremers and Urban. They found the boiling-point to be 210–212°, but worked with much smaller quantities.

The boiling-point of this ketone, $C_{10}H_{18}O$, is but a few degrees higher than that of menthone, (204–205° C.), the corresponding ketone richer by two hydrogen atoms.

Ketone Hydrosulphide.

Crystals of the hydrosulphide were very easily obtained by passing hydrogen sulphide into a solution of the ketone (1 volume) in alcohol (4 volumes) and subsequently adding strong ammonia water. On standing for twelve hours very fine needles appeared. These were separated by means of a force filter, washed with alcohol, and then dried on porous plates. The melting-point of the crystals was 212–215°. They were soluble in chloroform and hot methyl alcohol,

slightly soluble in ether, benzene, petroleum ether, and hot ethyl alcohol. The mother-liquid which possessed a decided *buchu* odor, was set aside for further crystallization. Two more crops of crystals were obtained. The melting-point of each was lower than that of the preceding one.

The several crops were mixed and dissolved in chloroform and allowed to crystallize. When dried they melted at 206–208°. A sulphur determination gave the following results:

0.2786 gram substance yielded 0.5802 gram $BaSO_4$ = 0.0796 gram S = 28.57 per cent.

Calculated for		Found.
$C_{10}H_{18}O.H_2S$	17.205 per cent.	28.57 per cent.
$C_{10}H_{18}O.2H_2S$	29.090 " "	

The result, although somewhat low, is decidedly in favor of the addition of 2 molecules of hydrogen sulphide.

Nitroso Derivative of Ketone.

Baeyer's formula for the preparation of nitrosopulegone was employed, but did not give a very large yield. Two cc. of the oil were dissolved in an equal volume of petroleum ether (boiling-point 65° C.) and then 1 cc. of ethyl nitrite added. The mixture contained in a test-tube is immersed in a freezing-mixture and stirred with a glass rod, which had been dipped in concentrated hydrochloric acid. After stirring for fifteen minutes the mixture was allowed to remain in the freezing-mixture for another fifteen minutes, when the white amorphous precipitate which had formed was removed with the aid of a force filter. After drying it melted at 115–115°.5 with slight decomposition, as shown by the compound turning brown. The yield was so small that no other work could be done with the compound.

Ketone and Phenylhydrazine Hydrochloride.

The hydrazone of the ketone was very easily prepared by dissolving 5 cc. of the oil in 12.5 cc. of alcohol and then 6.05 grams of phenylhydrazine hydrochloride and an excess of sodium bicarbonate added. On standing over night without heating, or heating with a reflux condenser on a water-bath for fifteen minutes and then cooling, the entire mass crystallized.

To purify the crystals they were dissolved in warm alcohol and allowed to recrystallize. Decomposition occurred so rapidly that only a very small quantity was obtained. This melted at 73.5–74°, with slight decomposition and evolution of a colorless gas. On cooling, the substance in the tube was of a bright green color. When remelted no further change was noticed. It melted at 72.5-73° and became green upon cooling. Fischer's precaution that in determining the melting-points of hydrazones they should be heated rapidly in order to avoid error, was carefully observed.

To obtain larger quantities for combustion a modification of the above method of preparation was adopted. The hot alcoholic solution, after being filtered, was gradually diluted with water until a slight turbidity resulted. After standing fifteen minutes a large quantity of fine silky crystals had separated. These were removed with the aid of a force filter, washed with dilute alcohol, drained and dried (melting-point 73.5–74° C.) The crystals decomposed within twenty-four hours with the evolution of gas. A spongy, dark-green, resinous mass remained.

The pure crystals gave the following results for nitrogen with the Will and Varentrapp method :

A. 0.2348 gram yielded 0.02387 gram N = 10.15 per cent.

B. 0.2330 gram yielded 0.02352 gram N = 10.095 per cent.

	Calculated for $C_6H_5NHN : C_{10}H_{16}$.	Found. I.	II.
N	11.57	10.15	10.095

Although somewhat too low, the above figures indicate that the formula $C_{10}H_{16} : NNHC_6H_5$ is correct and that a hydrazone is formed.

An attempt was also made to determine the nitrogen by means of the Kjeldahl method, but no satisfactory results were obtained. E. Lawes[1] finds that, contrary to previous reports, nitrogen in glucozone, phenylhydrazine, and antipyrine cannot be determined by the Kjeldahl method.

Ketone and Substituted Phenylhydrazine.

By using substituted phenylhydrazines it was hoped to obtain a more stable compound with the ketone, and the follow-

[1] Chem. Centralb., 1892, **2**, 628.

ing were tried: (*a*) acetylphenylhydrazine hydrochloride; (*b*) orthotoluylphenylhydrazine hydrochloride; and (*c*) paratoluylphenylhydrazine hydrochloride.

Both processes given under Δ^4-terpenehydrazone were tried with each substance; no positive results, however, were obtained.

Ketone and Nitrosochloride Reaction.

An attempt was made to prepare a nitrosochloride of the ketone (it having a double bond, Δ^4, in the ring). The formula used in preparing menthene nitrosochloride was employed. Several trials yield only negative results. During the experiments nitrous acid fumes were given off.

Reduction of Ketone.

In order to reduce the ketone, Beckmann's process was employed. 15 cc. of the oil (boiling-point 207–208°) were dissolved in 50 cc. of anhydrous ether. Metallic sodium in excess is gradually added and the mixture heated in a flask with a reflux condenser, on a water-bath, for four hours. The liquid portion, upon cooling, was decanted, and the residue washed with several successive portions of ether. Both portions of ether were placed in a separatory funnel and an equal volume of water added; the mixture was shaken occasionally and placed in a cool place for half an hour. The ethereal layer was then separated and allowed to evaporate spontaneously. Small, white crystals formed. These were separated from the reddish-brown oil, which had a decided odor of mint.

The oil was again heated in the same manner as above, excepting that instead of allowing the ethereal solution to evaporate it was distilled with water-vapor. The first portion which came over was entirely ether. The oil which distilled over was collected, dried, and exposed to a freezing-mixture. Nothing separated. The oil was light-yellow in color and of a minty odor.

A very heavy, reddish-brown, gummy residue remained in the distilling flask. It readily dissolved in hot alcohol, and from the solution crystals began to separate after standing several months.

None of the above compounds were obtained in sufficient quantities to work with. The experiment was repeated on a larger scale (using 150 cc. of the ketone and corresponding quantities of the other substances), and petroleum ether (boiling-point 65–70° C.) was used as the solvent. The same results were obtained as when anhydrous ether was used, except that crystals separated from the hot methyl-alcohol solution of the gummy residue very easily.

Oily Portion.

The oil which had a specific gravity of 0.9019 and $[\alpha]_D$ —0.8144° was fractionated (see Table XII). Most of it distilled over between 207–208° C., which fraction was colorless and of a mint-like odor. It is to be observed that this compound differs very slightly in its physical constants from the original ketone.

Molecular Coëfficient of Refraction.

This physical constant was determined by means of Pulfrich's total reflectometer, and calculated from the following formula for the coëfficient of refraction (according to Lorentz),

$$\left(R = \frac{n^2 - 1}{(n^2 + 2)\,d}\right)$$

in which

n = index of fluid examined (obtained from tables for refractometer) from angles read.

d = density of fluid examined.

R = coëfficient of fluid.

M = molecular weight of fluid examined.

MR = molecular coëfficient of fluid examined.

Observed : $n = 1.466921$ (20° C).

$d = 0.9103$.

Then $R = 0.304769824$.

M, in the case of the supposed alcohol = 154.

M, in the case of the original ketone = 152.

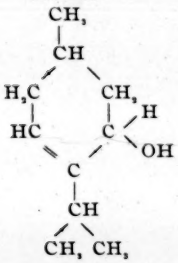
Then $MR = 46.93$ for the alcohol and 46.36 for the ketone.

The factors used in determining the molecular refraction according to Conrady are :

1. C (in C—C) = 2.501 ;
2. C (in C=C) = 1.707 additional ;
3. O (in O—H) = 1.521 ;
4. O (in C=O) = 2.287 ;
5. H = 1.051.

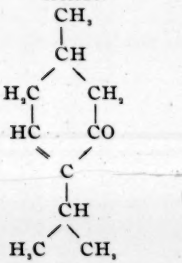
From these factors the calculated molecular refraction would be :

Alcohol.



C_{10}	(1)	25.01
	(2)	1.707
H_{18}	(3)	18.908
O	(4)	1.521
		47.146

Ketone.



C_{10}	(1)	25.01
	(2)	1.707
H_{16}	(3)	16.816
O	(4)	2.287
		45.820

	Alcohol.	Ketone.
Calculated	47.146	45.820
Found	46.935	46.325

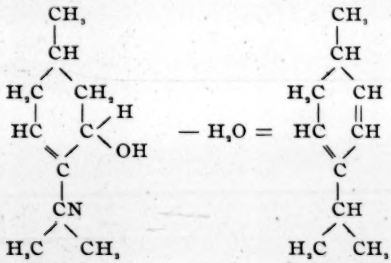
The figures seem to be in favor of the alcohol formula, but they do not vary greatly from the calculated results for the ketone. Chemical reactions seem to indicate that the supposed alcohol consists mainly of unchanged ketone.

Dehydration of Alcohol, $C_{10}H_{18}O$.

The supposed alcohol was treated the same as under *B* in the dehydration of menthol. The resulting oil, when fractionated, distilled over for the most part between 204°–206°, which fraction had a specific gravity of 0.9100 and $[\alpha]_D$— 1.3919°. All of the fractions were colorless and possessed a mint-like odor.

Nitrochloride Reaction.

The above compound, which was supposed to be the hydrocarbon $C_{10}H_{16}$ ($\Delta^{2,4}$-Terpadiene), formed according to the following equation:



Alcohol. Δ^4-Terpene-3-ol.

Hydrocarbon. $\Delta^{2,4}$-Terpadiene.

was treated with ethyl nitrite, concentrated hydrochloric acid, and glacial acetic acid, but no crystals were obtained upon several repeated trials.

Combustion of the oil gave the following results:

A. 0.2147 gram substance yielded
0.5918 gram CO_2 = 0.1614 gram C = 75.13 per cent. C.
0.2075 gram H_2O = 0.02305 gram H = 10.74 per cent. H.

B. 0.1991 gram substance yielded
0.5210 gram CO_2 = 0.1421 gram C = 71.39 per cent. C.
0.1925 gram H_2O = 0.0214 gram H = 10.75 per cent. H.

C. 0.1909 gram substance yielded
0.5228 gram CO_2 = 0.1426 gram C = 74.70 per cent. C.
0.1848 gram H_2O = 0.0205 gram H = 10.77 per cent. H.

	Calculated for $C_{10}H_{18}$.	Found. I.	II.	III.
C	88.24	75.13	71.39	74.70
H	11.76	10.74	10.75	10.77

That the oil cannot be a hydrocarbon is certain from the the above figures, since they admit of nearly 15 per cent. of oxygen.

Further proof was found in the fact that both an oxime (melting-point 67–68° C.) and a hydrosulphide (melting-point 212-214°) were obtained.

Crystals Obtained during Process of Reduction of Ketone.

The several lots of crystals which separated showed varying melting-points. All were, therefore, recrystallized from hot methyl alcohol, when they showed a melting-point of 160–162° C. Upon analysis the following results were obtained:

A. 0.2445 gram substance yielded
0.6451 gram CO_2 = 0.1759 gram C = 71.96 per cent. C.
0.2384 gram H_2O = 0.0265 gram H = 10.82 per cent. H.

B. 0.2024 gram substance yielded
0.5297 gram CO_2 = 0.14445 gram C = 71.86 per cent. C.
0.1993 gram H_2O = 0.02215 gram H = 10.94 per cent. H.

A test for sodium was made, but no appreciable amount was found. 0.2213 gram, after ignition, left no perceptible residue. Wallach, in the reduction of carvone to dihydrocarveol obtained a pinacone. These results agree neither with the formula for the alcohol, $C_{10}H_{17}OH$, nor for the corresponding pinacone. Molecular-weight determinations of this substance will next be made. The investigation along other lines will also be continued.

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ON TETRAMETAPHOSPHIMIC ACID.

By H. N. Stokes.

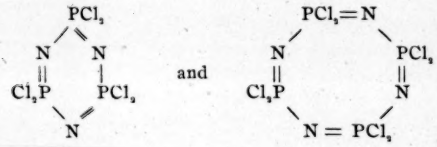
Trimetaphosphimic acid and its decomposition-products have been described in the preceding article on the phosphorus nitrogen compounds.[1] In the present paper some account is given of the next higher member of the series, *tetrametaphosphimic acid*, $P_4N_4O_8H_8$, which results from the decomposition by water of tetraphosphonitrilic chloride, $P_4N_4Cl_8$.[2] The molecular weight of the chloride having been established with certainty, that of the acid follows directly. Although the free acid crystallizes with 2 molecules of water, the silver salts and the acid potassium and ammonium salts are anhydrous and conform to the above formula.

Notwithstanding the proximity of these two acids in the series, and the general similarity of the chloronitrides from which they are derived, they differ exceedingly, trimetaphosphimic acid being extremely soluble, uncrystallizable, undergoing rapid spontaneous decomposition, and yielding but two series of salts; while tetrametaphosphimic acid is very difficultly soluble, highly crystalline, permanent when dry, offers marked resistance to the action of acids and forms three series of salts, $P_4N_4O_8H_4M'_4$, $P_4N_4O_8H_5M'$, and $P_4N_4O_8M'_8$. Those metals which form insoluble salts are precipitated from solutions of their chlorides or nitrates even by the free acid, but a very slight excess of either being required to make the precipitation complete. As is the case with trimetaphosphimic acid, the eight-atom silver salt exists in a white and a yellow modification, the former, however, being very unstable; these may be regarded as corresponding to the tautomeric forms $(PN(OH)_2)_4$ and $(PO.NH.OH)_4$. Under the action of stronger acids it is ultimately converted into orthophosphoric acid and ammonia, but its great stability, and the instability of the intermediate products, have rendered the isolation of the latter impossible.

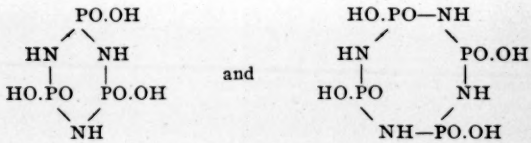
Experimental data for a discussion of the constitution of the acid are therefore almost wholly wanting. Presumably the phosphorus atoms in the nucleus P_4N_4 are united by nitrogen atoms, but whether they constitute a ring of eight

[1] This Journal, 18, 629. [2] *Ibid.*, 17, 275; Ber. d. chem. Ges., 28, 437.

atoms cannot be decided definitely in the absence of intermediate decomposition-products. It is quite likely that the reason of the greater stability of the acid may be found in steric considerations, and in this connection it is interesting to observe that while $P_4N_4O_8H_8$ is much more stable than $P_3N_3O_6H_6$, the reverse is true of the chloronitrides, for while $P_4N_4Cl_8$ also resists the action of boiling water and can be distilled with steam, it is perceptibly easier to saponify than $P_3N_3Cl_6$. If we assume the formulas



for the chloronitrides, and



for the acids, it is obvious that the nitrile configuration is more stable in a ring of six than in one of eight atoms, while for the group —NH—PO(OH)—NH— the reverse is true. The same appears in the different action of aqueous ammonia on the chloronitrides, two atoms of chlorine in $P_3N_3Cl_6$, and two only, being readily replaced by NH_2, forming a stable chloramide, while $P_4N_4Cl_8$ under the same conditions gives no chloramide, but the ammonium salt of tetrametaphosphimic acid.[1]

Experimental Part.

Preparation by Tetrametaphosphimic Acid.—Tetraphosphonitrilic chloride can be saponified by alcoholic alkalies, but the yield of tetrametaphosphimic acid is poor, owing to the formation of ethers, which, however, can be decomposed by

[1] This JOURNAL, 17, 286, 290.

prolonged treatment. Satisfactory results are obtained by using an ethereal solution, which is agitated, in the manner described under tetrametaphosphimic acid, with either water, ammonia or a solution of ammonium acetate.

Decomposition by Water.—As tetrametaphosphimic acid is not perceptibly attacked by cold hydrochloric acid, water may be used when it is desired to obtain the free acid directly. One part $P_4N_4Cl_8$ is dissolved in 15 volumes alcohol-free ether and gently agitated with 5 volumes water. Within half an hour needles of the free acid begin to separate from the aqueous portion, and after many hours the latter has become converted into a thick pasty mass of needles suspended in dilute hydrochloric acid. Chlorhydrines are formed as intermediate products, and these remain dissolved in the ether. It is not necessary to continue the agitation until they are completely decomposed; as soon as a few drops of the ether leave a residue wholly soluble in water, the ether is decanted and the aqueous portion filtered, the crystals being washed with 10-per cent. hydrochloric acid or alcohol. The ethereal portion, containing the chlorhydrines, is evaporated cautiously. The chlorhydrines which remain as an oil from which crystals separate after complete removal of the ether, are dissolved in a little cold water and warmed, with addition of dilute hydrochloric acid, in which tetrametaphosphimic acid is much less soluble than in pure water. The separation of the acid is nearly complete after a few minutes. This portion is better crystallized than that obtained directly, but is otherwise the same. The acid may be recrystallized from hot water, but this is quite unnecessary. Yield, about theoretical.

Decomposition by Ammonia.—The ethereal solution of the chloronitride is shaken for a short time with aqueous ammonia. This does not give chloramide as is the case with $P_3N_3Cl_6$, but produces at once neutral ammonium tetrametaphosphimate, $P_4N_4O_8H_4(NH_4)_4+4H_2O$, which is precipitated by adding alcohol and washed with dilute alcohol. The decomposition is complete in a few minutes.

Decomposition by Ammonium Acetate.—One part chloronitride, dissolved in 15 volumes ether, is agitated with a solution of 4 parts ammonium acetate in 8 parts water. After

several hours crystals begin to separate. The final product is a mixture of acid ammonium salt with some neutral salt and some free acid, and is nearly insoluble in the strong salt solution. It is washed with alcohol, dissolved in dilute ammonia and reprecipitated by alcohol. Yield, theoretical. Ammonium acetate is to be preferred to sodium acetate, as the sodium salt does not precipitate well with alcohol.

Chlorhydrines.—None of these were isolated. The oil left on distilling off the ether solidifies to plates as soon as the ether is completely removed. The crystalline substance is much more soluble in ether than the chloronitride, even momentary exposure to ether-vapor causing it to liquefy. It dissolves in cold water to a clear solution from which, in a few minutes, or sooner on warming, tetrametaphosphimic acid is deposited. On one occasion the flask containing the chlorhydrines was placed in hot water and a current of dry air passed through. Some hydrochloric acid was given off, and on treatment with water incomplete solution occurred, a portion being converted into a sandy powder, which, under the microscope, was seen to consist of short spindle-shaped crystals. This acid was insoluble in boiling water, and warm ammonia converted it without dissolving into an acicular ammonium salt, difficultly soluble in water and insoluble in an excess of ammonia; nitric acid dissolved this salt, which was reprecipitated by ammonia in a bulky amorphous form like precipitated alumina, which quickly changed to needles. This ammonium salt was very slowly attacked by hot concentrated sulphuric acid and contained 27.96 per cent. phosphorus and 13.28 per cent. nitrogen (P : N = 4 : 4.2). Lack of material prevented further study of this finely crystallized acid, of the nature of which I can form no conjecture.

Tetrametaphosphimic Acid, $P_4N_4O_6H_8 + 2H_2O$.—The free acid may be prepared by the first method above described. It is not readily obtained pure by decomposing most of its soluble salts, as even in the presence of a large excess of acid more or less acid salt is deposited. Thus on dissolving neutral ammonium salt and adding a large excess of hot 5-per cent. nitric acid, nearly pure acid salt was obtained. It may also be prepared by boiling the silver salt with much water, con-

taining about the requisite amount of hydrochloric acid for its decomposition, and precipitating by further addition of the same acid to the filtrate.

The analytical methods are the same as those employed for trimetaphosphimates, but much longer heating with strong sulphuric acid is necessary, because of its greater stability.

Analyses of four air-dried preparations gave :

	Calculated for $P_4N_4O_8H_8 + 2H_2O$.	Found. (1)	(2)	(3)	(4)
P	35.23	35.01	35.27	35.38	35.20
N	15.94	15.93	....	15.99	15.92
H	3.41	....	....	3.55	3.59

(1) P : N = 4 : 4.02.

(3) P : N : H = 4 : 4.06 : 12.43. From chlorhydrine.

(4) P : N : H = 4 : 4 : 12.64. First method, from aqueous portion.

The crystal water is not given off *in vacuo* over sulphuric acid. At 100° it loses weight rapidly, then slowly, but the total loss never reaches the theoretical, a portion of the water being taken up in producing intramolecular changes.

Loss calculated for $2H_2O$	10.22
(1) Loss after 24 hours (weight constant)	9.37
(2) Loss after 78 hours (weight constant)	8.91

If rapidly heated to 130–40° the loss is still less, and is soon replaced by a gain ; after thirty hours at this temperature a net *increase* of 11.15 per cent., corresponding to somewhat more than 2 molecules H_2O was observed, which must have come from the atmosphere. The product consisted of unchanged acid, with ammonium phosphate and apparently pyrophosphate.

Tetrametaphosphimic acid forms colorless needles, either single or in radiating groups, and visible without a lens ; they appear to consist of flat rectangularly terminated prisms. 100 parts water at 20° dissolve 0.64 part crystallized acid ; in boiling water it is somewhat more soluble, but is insoluble in alcohol. From its saturated aqueous solution it is partially precipitated by adding one of the stronger acids, and more rapidly if heated ; 100 parts by weight of 10-per cent. nitric acid at 20° dissolve only 0.26 part of the crystallized acid, but

on decomposing its salts in the cold by an excess of acid, it frequently dissolves completely and separates out later. Its saturated aqueous solution does not coagulate albumen. Boiling alkaline solutions cause no evolution of ammonia. Its stability towards acids is illustrated by the following: 0.1 gram, dissolved in 200 cc. water with 8 cc. strong nitric and some hydrochloric acid, was evaporated to dryness on the water-bath, whereby a large part was recovered unchanged; ten minutes heating would have sufficed for the total decomposition of the same quantity of trimetaphosphimic acid. Nitrous acid has no perceptible action.

Di-Potassium Tetrametaphosphimate, $P_4N_4O_8H_6K_2$.—The free acid dissolves easily in cold dilute caustic potash; on strongly acidifying with acetic acid the solution remains clear, but on warming the above salt is deposited as a heavy sandy powder, consisting of microscopic thick rectangular (quadratic?) prisms with basal planes. It is very difficultly soluble even in boiling water.

The air-dried substance lost nothing at 100° and gave:

	Calculated for $P_4N_4O_8H_6K_2$.	Found.
P	31.61	31.26
K	19.93	20.05

P : K = 4 : 2.03.

The tetra-potassium salt formed large flat obliquely terminated plates, very soluble, and was not isolated.

Tetra-Sodium Tetrametaphosphimate, $P_4N_4O_8H_4Na_4 + 2\frac{1}{2}$ (?) H_2O.—The acid is suspended in a little water, and an excess of dilute caustic soda added, whereby complete solution occurs. The separation of the neutral salt soon begins in the form of obliquely terminated flat prisms, sometimes single, sometimes in twins or quadruplets; the filtrate deposits more on heating, but in imperfect forms, broader at one end than at the other. Sometimes nothing separates from the alkaline solution until it is heated. On the contrary, strong caustic soda converts the solid acid in the salt without dissolving it. The salt is rather difficultly soluble in cold, quite easily in hot water, but much less soluble in the presence of an excess of alkali, and the latter throws it down from its saturated aqueous solution. Sodium carbonate gives the same salt.

The substance, pressed out without washing and dried *in vacuo*, lost nothing at 100° and gave :

	Calculated for $P_4N_4O_8H_4Na_4 + 2\frac{1}{2}H_2O$.	Found. (1)	(2)
P	27.62	27.61	27.71
Na	20.50	21.23	20.80

(1) P : Na = 4 : 4.14 ; (2) P : Na = 4 : 4.05.

Alcohol precipitates this salt in a slimy form, which filters with difficulty.

A solution of the tetra-sodium salt, strongly acidified with acetic acid gave a deposit of granules, probably the acid salt. A salt with more than 4 atoms of sodium[1] was not observed.

Tetra-Ammonium Tetrametaphosphimate, $P_4N_4O_8H_4(NH_4)_4 + 4H_2O$.—Strong ammonia converts tetrametaphosphimic acid into this salt without dissolving it ; from its solution in weaker ammonia it is precipitated by alcohol. It usually forms well developed flat monoclinic prisms with pinakoid and basal planes, the base being occasionally replaced by a set of many small planes. It is easily soluble in water, but difficultly in strong ammonia. Its solution undergoes partial decomposition into acid salt on evaporating. It loses nothing *in vacuo*, and analysis gave :

	Calculated for $P_4N_4O_8H_4(NH_4)_4 + 4H_2O$. (1)	Found. (2)	(3)
P	27.19	27.12	....	27.25
N	24.61	24.74	....	24.66
H	6.15	....	5.94	....

(1). P : N = 4 : 8.12 ; (3). P : N = 4 : 8.00.

Di-Ammonium Tetrametaphosphimate, $P_4N_4O_8H_8(NH_4)_2$.—This salt forms whenever a solution of the neutral salt is strongly acidified, and was at first mistaken for the free acid, which it somewhat resembles. It forms four- and six-sided prisms with base (tetragonal ?), closely resembling the acid potassium salt and, like this, is very difficultly soluble even in boiling water. It separates on heating a solution of the neutral salt with acetic acid in excess (Analyses 1 and 2); or with a stronger acid, in which case it may be slightly contaminated with free acid. The preparation under Analysis 3

[1] Compare the behavior of trimetaphosphimic acid toward excess of alkali.—This JOURNAL, 18, 642.

was crystallized from a large excess of hot 5-per cent. nitric acid. It contains no crystal water. Analysis gave:

	Calculated for $P_4N_4O_8H_8(NH_4)_2$.	Found. (1)	(2)	(3)
P	35.42	34.41	35.10	35.20
N	24.04	24.32	24.33	23.17

$$P : N \begin{cases} (1) = 4 : 6.26 \\ (2) = 4 : 6.15 \\ (3) = 4 : 5.82 \end{cases}$$

Barium Tetrametaphosphimate, $P_4N_4O_8H_4Ba_2 + 2H_2O$.—A solution of the di- or tetra-ammonium salt in 500 parts cold or, better, boiling water is precipitated by an excess of barium chloride. The salt forms a voluminous precipitate consisting of microscopic needles, branched or forked, insoluble in water, and undecomposed by acetic acid. These have approximately the composition of neutral salt, with a slight deficiency of barium.

The air-dried salt lost nothing at 100° and gave:

	Calculated for $P_4N_4O_8H_4Ba_2 + 2H_2O$.	Found. (1)	(2)
P	20.28	20.17	20.18
Ba	44.83	42.91	42.39

(1). P : Ba = 4 : 1.93, from acid ammonium salt.

(2). P : Ba = 4 : 1.90, from neutral ammonium salt.

Basic barium salts of indefinite properties seem to exist, but no indication of an acid salt could be obtained.

No satisfactory results were obtained with *magnesium* salts, a large variety of crystalline and amorphous precipitates being obtained under different conditions.

Manganese salts give with free tetrametaphosphimic acid a flocculent precipitate of neutral manganese tetrametaphosphimate; on adding a mineral acid this is decomposed, according to the proportion of the latter, into acid salt or free acid, or a mixture of both. The acid salt forms handsome pinkish rectangular plates, often superposed at various angles, and is one of the most characteristic salts obtained.

Ferric chloride gives no precipitate with a cold dilute solution of the neutral ammonium salt; on warming a white amorphous precipitate forms, which is soluble only on warm-

ing with much hydrochloric acid, from which solution, on cooling, the free acid separates.

Tetra-Silver Tetrametaphosphimate, $P_4N_4O_8H_4Ag_4$.—If to a cold solution of tetrametaphosphimic acid silver nitrate be added the resulting precipitate is white, curdy, and, under the microscope, granular or amorphous; formed in the presence of some alcohol it is even flocculent. These amorphous precipitates, after drying, slowly change to needles, and this occurs at once if they be boiled under water. The salt is obtained at once in crystalline form if a slight excess of silver nitrate be added to a hot solution of tetrametaphosphimic acid in 200–300 parts water. It requires but a slight excess of silver nitrate to bring about complete precipitation, the liberated nitric acid exercising a scarcely perceptible solvent action. Neutral ammonium salt may be used, but the addition of a little nitric acid is essential, otherwise the product is yellowish from contamination with the eight-atom silver salt.

When precipitated hot the salt sometimes consists of thick needles with tufts or brushes at each end, sometimes of long pointed plates, more rarely of rhombic plates, and in no case are they well formed or very characteristic. An acid salt could not be obtained, but the neutral salt always shows a slight deficiency of silver.

The air-dried substance lost nothing at 100° and gave:

	Calculated for $P_4N_4O_8H_4Ag_4$.	Found. (1)	(2)	(3)	(4)	(5)	(6)
P	16.68	16.78	17.04	17.04	16.68	16.84	16.74
N	7.55	....	....	....	....	....	7.62
Ag	58.04	....	57.06	56.13	57.09	57.09	57.40

$$P : Ag \begin{cases} (2) = 4 : 3.85 \\ (3) = 4 : 3.79 \\ (4) = 4 : 3.94 \\ (5) = 4 : 3.90 \end{cases} \qquad (6)\ P : N : Ag = 4 : 4.02 : 3.95$$

Octa-Silver Tetrametaphosphimate, $P_4N_4O_8Ag_8$.—If an ammoniacal solution of a tetrametaphosphimate be added to an excess of silver nitrate, a yellowish flocculent precipitate forms, which is insoluble in ammonium nitrate and which does not change on boiling under its mother-liquor or under pure water. On drying at 100° it became grayish olive-colored,

apparently because of the separation of some silver oxide. It gave the figures under 1, 2 and 3.

If a solution of a neutral tetrametaphosphimate be added to ammoniacal silver nitrate containing the least possible excess of ammonia, a nearly white flocculent precipitate forms in small amount, which is soluble in ammonium nitrate solution on gently warming; from this solution an orange-yellow semi-crystalline body is thrown out on boiling for a moment. The latter is obtained in greater abundance by boiling the original filtrate from the silver-nitrate precipitate. It seems to be merely the crystalline modification of the above amorphous yellow salt. It gave the figures under Analysis 4. The nearly white modification is obtained in greater amount by using a solution of silver oxide in ammonium nitrate solution. It shows a considerable deficiency of silver (P : Ag = 4 : 6.7) and seems to be less stable than the corresponding white hexa-silver trimetaphosphimate, as it cannot be obtained entirely free from the yellow modification. The yellow form also shows a slight deficiency of silver, and unlike the trimetaphosphimate, it cannot be converted into a red form.

The yellow salts, dried at 100°, gave:

	Calculated for $P_4N_4O_5Ag_6$.	Found. (1)	(2)	(3)	(4)
P	10.59	10.47	10.88	10.80	10.89
Ag	73.69	71.86	71.60	71.96	72.21

P : Ag { (1) = 4 : 7.90; (2) = 4 : 7.57; (3) = 4 : 7.66; (4) = 4 : 7.63 }

1–3, amorphous.
4, semi-crystalline.

U. S. GEOLOGICAL SURVEY,
WASHINGTON, July, 1896.

NOTE.

AUGUST KEKULÉ.

Friederich August Kekulé von Stradonitz, one of the greatest chemists of this century, died on the 13th of July last. Kekulé was born on the 7th of September, 1829, at Darmstadt. As in early life he exhibited marked excellence in mathematics and drawing, his parents wished him to become an architect, but, being attracted by the lectures of Liebig, he turned to

chemistry. Later he went to Paris, where he worked with Dumas, Würtz, and Gerhardt. Then he went to London, where he enjoyed the friendship of Williamson. In 1856 he became Privatdocent at Heidelberg; in 1858 he was appointed professor in the University of Gent; and in 1865 he became Hofmann's successor in the University of Bonn, where he remained until the end of his life—a period of thirty-one years.

Kekulé has exerted a powerful influence upon the thoughts of chemists during the past thirty years. He first showed how the general application of ideas, previously put forward by Frankland, Williamson, and others, helped to clear up many problems of constitution that were not clear in the light of the theory of types. He showed that the four types to which chemists were then referring chemical compounds for purposes of classification were themselves to be referred back to fundamental differences between the typical atoms, and that it was possible to go beyond the types—"back to the elements themselves"—and show how the elements are combined. The conceptions of constitution now held were worked out in a clear way for the first time by Kekulé, and, while these conceptions were not original with him, it is to him that we owe their general acceptance.

Kekulé's name is most frequently heard in connection with the famous hypothesis of benzene, proposed by him in 1865. It is generally recognized that this hypothesis has contributed more than any other single thought to the progress of chemistry during the past thirty years. In 1890 the chemists of the world met at Berlin, under the auspices of the German Chemical Society, to do honor to Kekulé by celebrating the twenty-fifth anniversary of the birth of the benzene theory. No other chemist has been thus honored during his life-time. The account of the meeting[1] is most interesting to every chemist; and the reading of it will show in what esteem Kekulé's work is held.

For years past Kekulé has not been very actively engaged in experimental work. Perhaps the principal reason for this was his poor health. When he began his career Liebig told him that he would never succeed unless he gave himself up to his work to such an extent as to ruin his health. Whatever effect this may have had upon him, it is certain that overwork in his early days did ruin his health.

A full account of Kekulé's life will appear in the *Berichte der deutschen chemischen Gesellschaft.*

[1] Ber. d. chem. Ges., **23**, 1205–1312.